HELSINKI UNIVERSITY OF TECHNOLOGY

Department of Chemical Technology

Qian Chen

CHEMICAL THERMODYNAMICS OF CARBON DIOXIDE WITH MIXED AQUEOUS ALKANOLAMINE SOLUTIONS AND METALCARBONATES

Thesis for the degree of Master of Science in Technology

Espoo, 20 December 2004

Supervisor:

Professor Simo Liukkonen

Instructors:

Dr. Justin Salminen

Lic. Sc. Tech. Petri Kobylin

PREFACE

This work is concerned with the equilibrium solubilities and chemistry of carbon dioxide in alkanolamine, ionic liquids and metal carbonate systems. It is part of the TEKES project "Total energy models, properties and environmental impact of greenhouse gases in chemical processes." (Kokonaisenergiamallit sekä kasvihuonekaasujen ominaisuudet prosesseissa ja niiden ympäristövaikutukset''.) The work was carried out at Helsinki University of Technology in the laboratory of Physical Chemistry and Electrochemistry during 1.2 – 20.12.2004 in co-operation with University of California Berkeley.

I wish to express my sincere gratitude and appreciation to Professor Simo Liukkonen throughout my graduate work, Dr. Justin Salminen (HUT and UCB), and Lic. Sc. Tech. Petri Kobylin (HUT) for helping and giving their intelligent guidance during the course of this work. I would like also to thank M.Sc. (Tech.) Claudia Dell'Era (HUT) for giving her valuable advisement in this work. Thanks are due to the personnel of laboratory of Physical Chemistry and Electrochemistry in HUT for their support in this work.

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My parents, my sister and my friends deserve my appreciation for their supporting and understanding.

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Qian Chen

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ABSTRACT OF MASTER'S THESIS

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Chemical thermodynamics of carbon dioxide with mixed aqueous alkanolamine solutions and metalcarbonates

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Supervisor

Prof Simo Liukkonen

Instructors

Dr. Justin Salminen
Lic. Sc. Tech. Petri Kobylin

The objective of this thesis is to investigate the solubilities and chemistry of carbon dioxide in alkanolamine, ionic liquids and metal carbonate systems. A general knowledge of CO_2 sources from both natural environment and industrial emissions, a variety of capture options to reduce CO_2 emissions, storage and utilisation methods are presented. Temperature, pressure, and composition dependence of CO_2 in MEA, DEA, MDEA, AMP, mixed alkanoamine solvents and ionic liquids have been studied. In addition CO_2 solubilities in multiphase system Na-Ca-Mg-Zn-Pb-Cd-H-Cl^--OH^--HCO_3^--CO_2-O_2 -H_2O at 25 °C have been investigated by thermodynamic model developed in this work.

A simple model for predicting acid gas vapour (CO_2 or CO_2 + H_2S) solubilities in MDEA at equilibrium under the condition of total gas loadings from 0.003 to 0.8, and temperature from 40 °C to 100 °C was used. Results of modelling of acid gas in MDEA, and CO_2 solubilities in salt chloride are in good agreements with the literature. In addition, Pitzer's activity coefficient model was used for calculating CO_2 solubilities in multiphase metalcarbonate systems in different temperatures by Gibbs energy minimization method. CO_2 solubilities in $PbCO_3$ - H_2O and $CdCO_3$ - H_2O differ a bit from the literatures mainly due to the variability of standard thermodynamic data.

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LIST OF SYMBOLS AND ABBREVIATIONS

LIST OF SYMBOLS

°C	Celsius degree
ΔP	pressure difference
H	Henry's constant
y_i	vapour-phase mole fraction
x_i	liquid-phase mole fraction
P	total pressure
P_i^*	vapour pressure of pure species *i* at the temperature of the system
γ_i	activity coefficient
a_i	activity of the component
T^V	temperature at vapour phase
T^L	temperature at liquid phase
P^V	pressure at vapour phase
P^L	pressure at liquid phase
μ_i^V	chemical potential of component at vapour phase
μ_i^L	chemical potential of component at liquid phase
f_i	fugacity of the components
ϕi	fugacity coefficient of species
$f_i^o(T, P)$	standard-state fugacity
$\mu_i^{oV}(T)$	standard chemical potentials at vapour phase
$\mu_i^{\phi L}(T, P)$	standard chemical potentials at liquid phase
m_i	molality of CO_2 molecular
p_{CO_2}	partial pressure of CO_2
wt %	weigh percentage
X^0_{Amine}	initial amine concentration
K	equilibrium constant
L_T	total loading of acid gases
α_{CO_2}	loading of CO_2

α_{H_2S}	loading of H_2S
R1, *R2*	groups of parameters
f(I)	modified Debye-Hückel term
I	ionic strength
B, θ	binary ion-ion parameters
C, ψ	ternary ion-ion parameters
K_{SP}	solubility product of sparing compounds
K_{ps0}^{I}	solubility product at a certain ionic strength
A_{ϕ}	osmotic Debye-Hückel parameter
λ_{ij}	second virial coefficients for species i and j
μ_{ij}	third virial coefficients for species i and j
$\Delta H°_f$	change of enthalpy
$S°$	entropy

superscript

°	Celsius degree
V	vapour phase
L	liquid phase
0	standard-state

subscript

i	pure species of chemicals
j	pure species of chemicals

LIST OF ABBREVIATIONS

GHG	greenhouse gas
ppmv	parts per million by volume
Gt	gigatonne (billion metric tons)
C	carbon
^{14}C	isotope of carbon

yr	year
CFCs	chlorofluorocarbons
HFCs	hydrofluorocarbons
PFCs	perfluorocarbons
IEA	International Energy Agency
OECD	Organisation for Economic Co-operation and Development
EU	European Union
CCS	Carbon dioxide Capture and Storage
MEA	monoethanolamine
DEA	diethanolamine
MDEA	N-methyldiethanolamine
AMP	2-amino-2-methyl-1-propanol
PSA	pressure swing adsorption
TSA	temperature swing adsorption
ESA	electrical swing adsorption
IGCC	Integrated Gasification Combined Cycle
EOR	enhanced oil recovery operation
MW	megawatt
BTX	Benzene, Toluene and Xylene
VLE	vapour/liquid equilibrium
RR'NH	alkanolamine
$RR'NCOO^-$	carbamate ions
ILs	ionic liquids
$[bmim][PF_6]$	1-n-butyl-3-methylimidazolium hexaflurophosphate
$[bmim][BF_4]$	1-n-butyl-3-methylimidazolium tetrafluoroborate
$[emim][Tf_2N]$	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
HUT	Helsinki University of Technology

1. INTRODUCTION

Carbon dioxide (CO_2) is always present in the atmosphere where its amount has been found to increase yearly. CO_2 is the most prevalent source of acidity in natural water (unperturbed by man) and causes minerals to dissolve in weathering process. Sources of CO_2 include volcanic emissions, respiration, fossil fuel combustion, decomposition of organic matter and precipitation of carbonates. CO_2 is one of the main greenhouse gas component in the atmosphere. It is responsible for over half the enhancement of the greenhouse effect, leading to changes in the climate.

A variety of technical options to reduce CO_2 emissions have been carried out world-wide, especially from use of energy since the largest single contribution to CO_2 emissions is from fossil fuels combustion. Reducing CO_2 emissions can be achieved through reducing the consumption of energy services; improving energy efficiency; fuel switching; enhancing the sinks for CO_2; use of renewable energy sources or nuclear power; and capture and storage of CO_2.

Nowadays reducing energy consumption and switching to low carbon fuels are considered as cost-effective techniques, and will deliver useful reductions in emissions. The natural sinks, like forests, could make a significant contribution as a short-term solution. Large reductions in emissions could be achieved by widespread switching to renewable energy or nuclear power. However, the capacities of renewable energy technologies and nuclear power have limitations to meet the increased demand of energy worldwide.

Capturing CO_2 and storing it underground has only recently been considered as a potential method of reducing emissions. The importance of this technology relies on the fact that currently about 85 % of the world's commercial energy is supplied by fossil fuels.[1] Rapid change to non-fossil energy sources would result in large disruption to the energy supply infrastructure, therefore with substantial consequences for the global economy.

Several technologies for CO_2 capture are expected to be suitable for current power generation technologies as well as for the future. Amine scrubbing technology used in the oil and chemical industries for removal of hydrogen sulphide and CO_2 from gas stream is one of the best techniques available for CO_2 capture. The commonly used alkanolamines are Monoethanolamine (MEA), N-methyldiethanolamine (MDEA), diethanolamine (DEA), 2-Amino-2-methyl-1-propanol (AMP), and mixed amine solvents. Cryogenic separation is widely used commercially for streams that already have high CO_2 concentration, but it is not used for more diluted CO_2 streams. Membrane development is required before they could be used on a significant scale for the capture of CO_2. But the extent to which their present high cost could be reduced is not clear, and solvent assisted membranes are being developed to combine the best features of membranes and solvent scrubbing. Capture of CO_2 by adsorption is most effective when the concentration in the gas in between 400 ppm and 15000 ppm in power stations. Ionic liquids that are commonly known as room temperature molten salts could potentially be used in CO_2 separation. Ionic liquids are also thermally stable up to approximately 250 ^{o}C and generally have no vapour pressure.

Carbonate minerals have played an important role in the geochemical evolution of Earth. Metalcarbonates, like $CaCO_3$, $MgCO_3$, $ZnCO_3$, $PbCO_3$, and $CdCO_3$ are sparingly soluble in water. Carbon dioxide gas can be used to dissolve and precipitate metal carbonate $M^{2+}CO_3^{2-}$ type salts from their chlorides utilizing CO_2 weak acid character and common anion feature of the buffering electrolytes like $NaHCO_3$ and K_2CO_3.

2. CO_2 EMISSIONS IN GENERAL

2.1 CO_2 in the nature

Carbon dioxide is a very important component of Earth's atmosphere, which has been present at a low concentration and acts as one of the major greenhouse gases (GHG). Carbon dioxide contributes about 26 % to the greenhouse effects.[2, 3] Carbon dioxide results from the combustion of organic matter if sufficient amounts of oxygen are present. It is also produced by various micro-organisms in fermentation and is breathed out by animals. Plants absorb carbon dioxide during photosynthesis, using both the carbon and the oxygen to construct carbohydrates.

The atmospheric CO_2 concentration was 353 ppmv (parts per million by volume) in 1990, it is about 25 % greater than the pre-industrial (1750-1800) value of about 280 ppmv. Carbon dioxide is increasing at about 1.8 ppmv per year due to anthropogenic emissions.[4]

The leading cause of anthropogenic carbon dioxide emission is releasing of burning carbon-containing fossil fuels such as oil, natural gas, and coals.

$$C\ (coke) + O_2\ (g) \rightarrow CO_2\ (g) \qquad (2.1)$$

The second major cause is deforestation accompanied by burning and biodegradation of biomass. During the long life time of CO_2 ranging from 50 to 200 years (depending upon the sinks) in the atmosphere, carbon dioxide readily absorbs infrared radiation and therefore contributes to global warming. [3, 4] According to the US Department of Energy, in 1990, from annual 7.4 Gt CO_2 emissions: 3.5 Gt/yr C (47 %) are released in the air, 2.2 Gt/yr C (30 %) is taken up by the oceans via the air, and 1.7 Gt/yr C (23 %) is captured on land by photosynthesis and other plant activity.[5]

The ocean is an important reservoir for taking up anthropogenic CO_2. CO_2 is much more soluble in seawater than in fresh water due to its high pH value (around pH~8).[1]

The following equilibrium reactions occurs during the dissolving of CO_2 in water.[6,7]

$$CO_2(g) \leftrightarrow CO_2(aq) \quad (2.2)$$

$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^- \text{ (bicarbonate ion)} \quad (2.3)$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \text{ (carbonate ion)} \quad (2.4)$$

Only 1 % of the CO_2 remains in molecular form and more than 90 % are in the form of the bicarbonate ion in seawater.[1]

The surface water temperature of natural water has an important effect on the solubility of CO_2. Figure 2.1[8] shows that the solubility of CO_2 in water decreases with the increasing temperature. Carroll et al[9] also calculated the solubility of CO_2 in water at 101.325 kPa, the 1000*mole fraction (x) is plotted as a function of temperature shown in figure 2.2.[9] It leads to the fact that relative warm surface waters of the sea are saturated with CO_2, but the colder deep waters of the world's oceans are unsaturated. [1, 8]

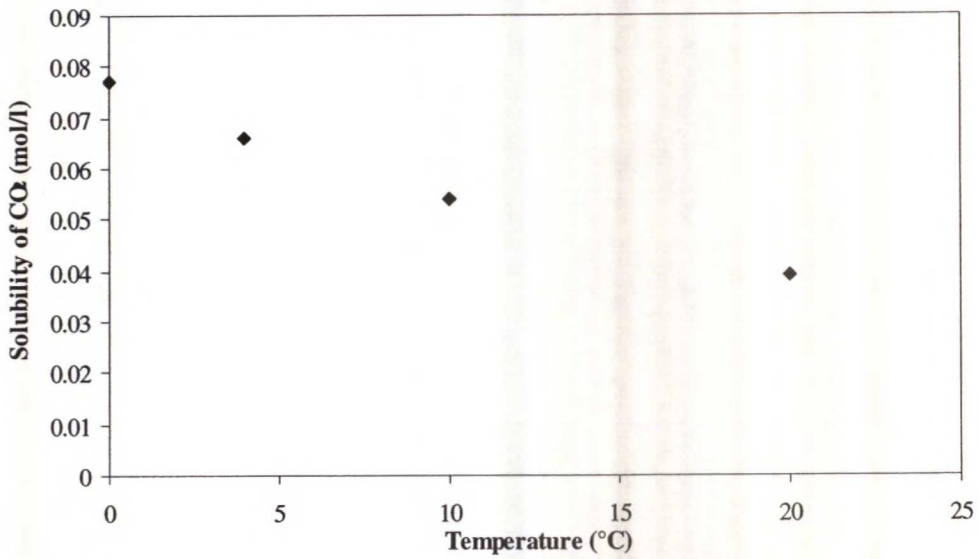

Fig. 2.1 Solubility of CO_2 in pure water as a function of temperature. [8]

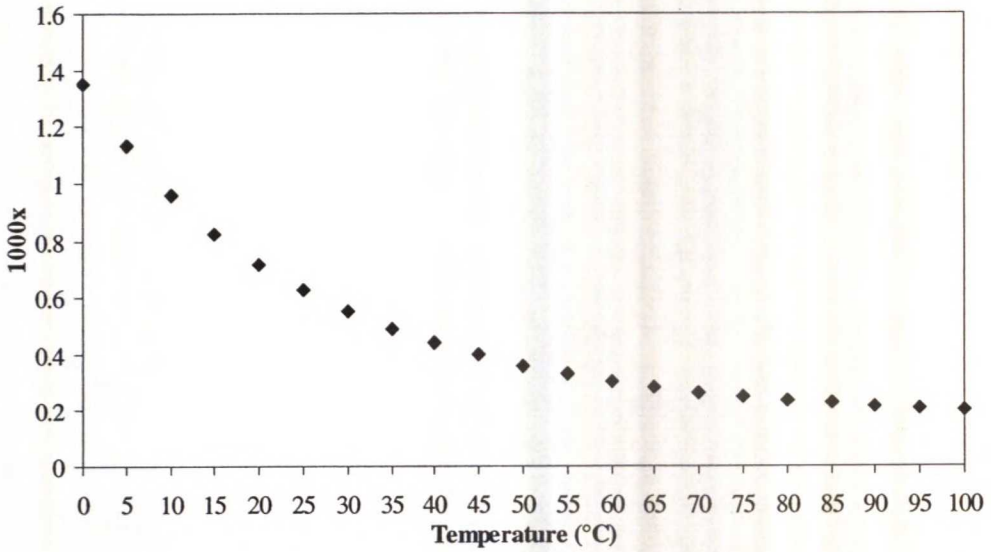

Fig. 2.2 Solubility of CO_2 in pure water at 101.325 kPa as a function of temperature.[9]

The increase of dissolved carbon dioxide in ocean water is smaller than in the atmosphere (only 2-3 percent until 1990). The driving force of CO_2 into ocean is expressed with net flux of CO_2, which is given by the product of a gas transfer coefficient and ΔP_{CO2} (the CO_2 partial pressure difference between ocean and atmosphere). The gas transfer coefficient increases with wind speed, and it is also dependent on water temperature. The study[4] shows that if the atmospheric CO_2 concentration increases by e.g., 10 %, the concentration of dissolved inorganic carbon in seawater increases by only about 1 % at equilibrium. Hence, the ocean is not a powerful natural sink for absorbing anthropogenic CO_2 when comparing the relative sizes of the reservoirs. The transporting of carbon from the surface to the deeper ocean layer is obtained by H_2O motions.[3,4]

Broecker and Peng [10] made the measurements for the radioactive isotope ^{14}C, it takes hundreds to about one thousand year for water at the surface to penetrate below the mixed layer of the major oceans. It is believed the first 100 meters in depth of the ocean is ideally mixed and in thermodynamic equilibrium with the air, therefore, it takes up significant amounts of anthropogenic CO_2.[5]

2.2. Industrial CO_2 emissions

2.2.1 Greenhouse Effect

The greenhouse effect is the process by which the atmosphere warms the Earth. When solar radiation reaches Earth's atmosphere, short-wave solar radiation can pass through the clear atmosphere, but long-wave terrestrial radiation emitted by the warm surface of the Earth is partially absorbed, and then re-emitted out to space by a number of trace gases in the cooler atmosphere. This process increases the energy to the lower atmosphere and the underlying surface, thus leads to a rising of surface temperature of the earth, which is well known as global warming. [3, 4]

The naturally occurring greenhouse gases include water vapour, carbon dioxide, methane, and nitrous oxide. In addition, man-made greenhouse gases include chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulphur hexafluoride (SF_6). The emissions of greenhouse gases have increased substantially due to industrialisation and changes in agriculture and land-use. [3]

Climate change is a highly complex problem, which has the potential to impact negatively on every sphere of life. The increase in carbon dioxide has been the most important factor to the climate change; it contributes about 60% of the increased radiative forcing over the last 200 years.[3] Figure 2.3 shows an increasing atmospheric concentration of CO_2 measured at Mauna Loa since 1958. On March 21, 2004, the reported value showed that the concentration of CO_2 reached 376 ppm in 2003.[3]

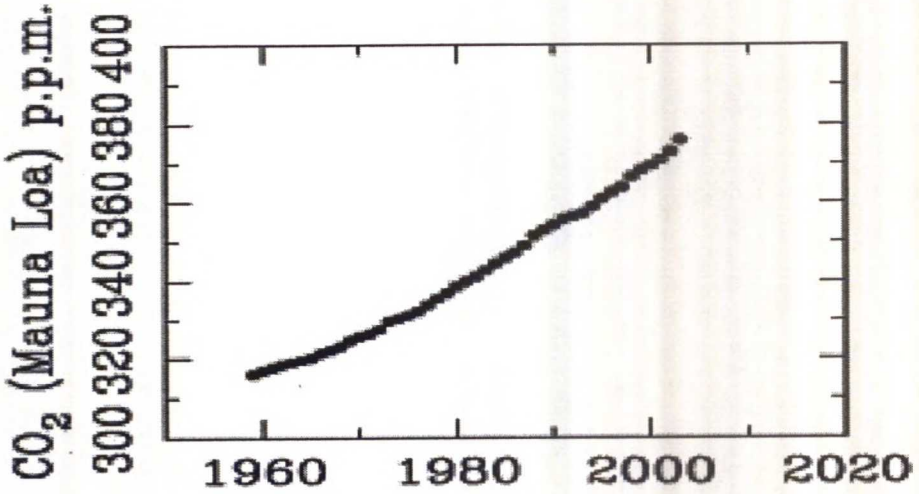

Fig. 2.3 CO_2 concentration measured at Mauna Loa, Hawaii since 1958 showing trends and seasonal cycle.[3]

The International Energy Agency Greenhouse Gas R&D Programme (IEA GHG) has collected some data on current CO_2 emissions from major anthropogenic sources both for regional stationary CO_2 emissions and for industrial manufacturing.[11] The quantities of stationary CO_2 emissions for each region in 2000 are shown in Figure 2.4. China accounts for 25 % (3.4 Gt / yr) of major CO_2 emissions in the world, then comes North America 20 % (2.69 Gt / yr) and OECD Europe 13 % (1.75 Gt / yr). The rest of the regions only emit less than 10 % of the total.

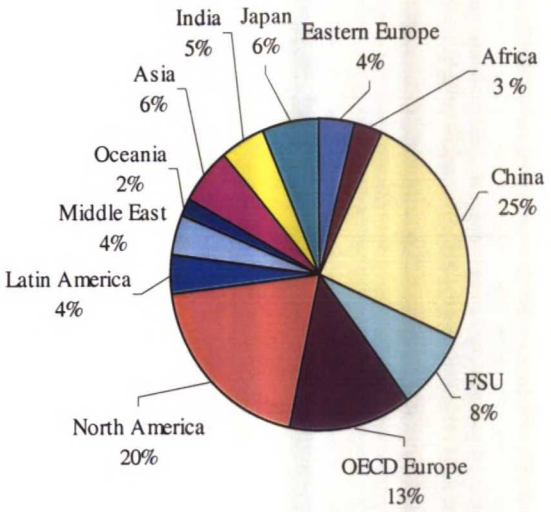

Fig. 2.4 CO_2 Emissions Sources by Geographical Region.[11]

The distribution of stationary CO_2 emission sources by industrial sectors is shown in Figure 2.5. Power plants dominate the leading emission at 54 % of the total. Cement industry accounts for 15 % as the second and followed by gas processing at 12 %.

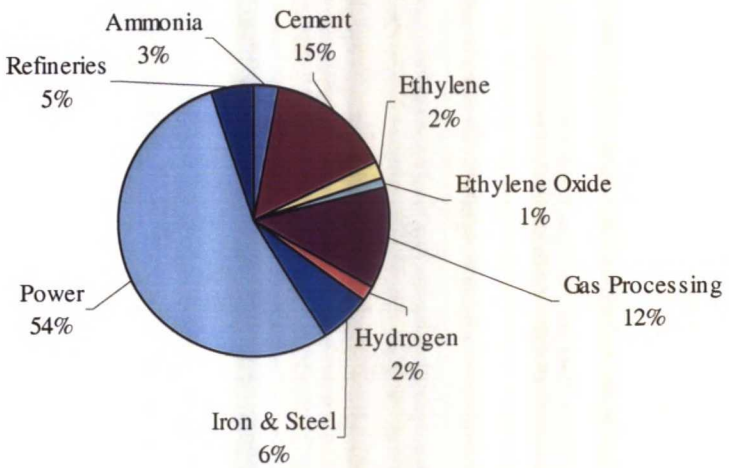

Fig. 2.5 Distributions of CO_2 Emission Sources by Industry Sector.[11]

2.2.2 The Kyoto target

Climate change and its deviating effects need urgent attention that is backed up by a broad understanding of political will and scientific findings. The 1992 United Nations Framework Convention is banding countries together to deal with pollution matters of the oceans, dry land degradation, damaging to the ozone layer, and the rapid extinction of plants and animals species. In 1997, government's responses to some growing public pressure are by adopting the Kyoto protocols, which is considered to be the most far-reaching agreement on environment and substantial development. [12]

The Protocol commits countries to reduce their collective emissions by at least 5 %. Each country's emission levels will be calculated as an average of the years 2008-2012. The protocol addresses the six main greenhouse gases. Cuts in three major gases – carbon dioxide, methane, and nitrous oxide – will be measured against a base year of 1990. Carbon dioxide is by far the most important gas, which is accounted for over four fifths of total greenhouse gas emissions from developed countries. As a result, emissions of CO_2 may need to be reduced by more than 60 % by 2100, in order to stabilize the atmospheric concentration of CO_2 at no more than 50 % above the current level.[13] Under the Protocol, targets can improve the ability of forests and other natural sinks to absorb carbon dioxide from the atmosphere.[12]

The overall 5 % target for developed countries is to be carried through cutting 8 % in European Union (EU), Switzerland, and most Central and East European states; 7 % in the US; and 6 % in Canada, Hungary, Japan, and Poland. New Zealand, Russia, and Ukraine are to stabilise their emissions, while Norway may increase emissions by up to 1 %, Australia by up to 8 % and Iceland 10 %. Internal agreements has been made inside the EU, these targets range from a 28 % reduction by Luxembourg and 21 % cuts by Denmark and Germany, 25 % increase by Greece and 27 % for Portugal. The emissions target for developing countries on how evolving the growth of global emissions has generated a great deal of intense debates.[12]

As the growing energy requirements in the future, switching from fossil fuels to hydrogen could dramatically reduce air pollution, hence, reduce the threat of greenhouse gases to climate change. Even though hydrogen generated from fuel cell emits no greenhouse gases, but the high cost brings the barrier to technical. Using steam and catalysts to break down natural gas into hydrogen and CO_2 is by far the cheapest way to produce hydrogen.[14] But the fact that capturing CO_2 from hydrogen production should be always implemented to meet Kyoto agreement for reducing greenhouse gases. As a result, the improved technology with low cost for capturing CO_2 is still a challenging task.[1]

However, it has been a long pause since the Kyoto protocol was signed in 11 December, 1997. Since it was always come up with economical and political issues, which opponents consider Kyoto protocol is to prevent the growth of the countries' economy. In 2004, Russia has signed the Kyoto protocol. By far, the United States has been one of the largest emitter of greenhouse gases; it still hasn't ratified the protocol yet.[3, 15]

3. REDUCTION AND UTILISATION OF CO_2 EMISSIONS

Carbon dioxide emissions can be reduced by several techniques. Reducing the consumption of energy is the most important method. Also using low carbon content fuels natural gas instead of coal, will lower CO_2 emissions. Using renewable energy or nuclear energy can contribute on CO_2 reductions. Forests, soils are the natural sinks, which could be enhanced to contribute CO_2 emissions from the atmosphere. The ocean storage of CO_2 is considered as an alternative. But due to the risk for harming marine ecosystem, it is not clear whether ocean storage would meet environmental regulations. However, the usage of any new technical options will be constrained by the economics, their technical performance, and eventually by thermodynamic restrictions.

Due to the fact that main CO_2 emissions is the combustion of fossil fuel, it can be concluded that controlling the CO_2 emissions in large scale- stationary sources will have largest impact on GHG emissions. This makes the importance of CO_2 capture and storage, which would enable the world to continue to use fossil fuels with reduced CO_2 emissions.[1,16]

3.1 Options for CO_2 capture

The technology of CO_2 capture and storage (CCS) prevents nearly 90 % of the fossil carbon from reaching the atmosphere. The capture of CO_2 can occur at base load power plant; at H_2 plant; and at coal-to-synfuels plant. Two steps are involved in performing the approach, first is pre-combustion capture of CO_2, then followed by geologic storage, in which the waste CO_2 is injected into subsurface geologic reservoir.[14] In addition, two other options can also be utilized for capturing CO_2 from fossil fuel combustion plant: post-combustion capture and oxyfuel combustion.[16]

3.1.1 Post-combustion capture

Post-combustion capture involves the separation of CO_2 from flue gas. At present the preferred technique is to scrub the gas steam using an amine solvent, which reacts with CO_2 to form a compound. After leaving the scrubber, the solvent is then heated

to break down the compound and release high purity CO_2, and CO_2-free amine is then reused. Post-combustion capture of CO_2 is widely used on coal- and oil-fired power stations to reduce SO_2 emissions as well.

Post-combustion capture process is shown in Figure 3.1. With this process, a large amount of energy is needed to regenerate the solvent and to compress the CO_2 for the transport, which minimise the net electricity output of the plant. In long-term goals, these developments offer significant reductions in capture costs and improvements to electricity generation efficiency. But the post-combustion capture does have disadvantages. The low concentration of CO_2 in power station flue-gases means that large volumes of flue-gases have to be treated. This leads to large equipments energy consumption. [1,16]

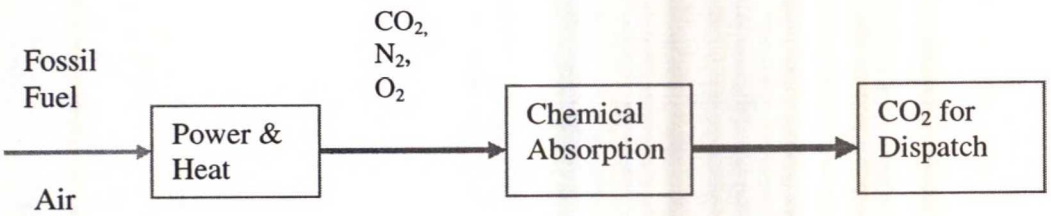

Fig. 3.1 Schematic diagram of the post-combustion capture process.[16]

3.1.2 Pre-combustion capture

Pre-combustion capture involves reaction of the fuel with oxygen or air, and in some cases steam, to give mainly carbon monoxide and hydrogen. The carbon monoxide is reacted with steam under the catalytic condition and converts to CO_2 and hydrogen. The CO_2 is then separated and the hydrogen is used as fuel in a gas turbine combined cycle plant. Figure 3.2 shows the process of pre-combustion capture. This process can be applied to natural gas, oil or coal, but additional equipment is needed to remove sulphur compounds and particulate in the oil and coal fuels.

Comparing pre-combustion separation with post-combustion, the advantage is that pre-combustion separation produces a smaller volume of rich-CO_2 gas at high pressure. This makes the gas separation plant smaller reducing the capital cost. Higher concentration of CO_2 enables less selective gas separation techniques such as, physical solvents or adsorption/desorption is used, which improve energy efficiency. Besides that, in the long run, the hydrogen produced in the process has significant future potential to be used to generate electricity in a fuel cell.[1, 16]

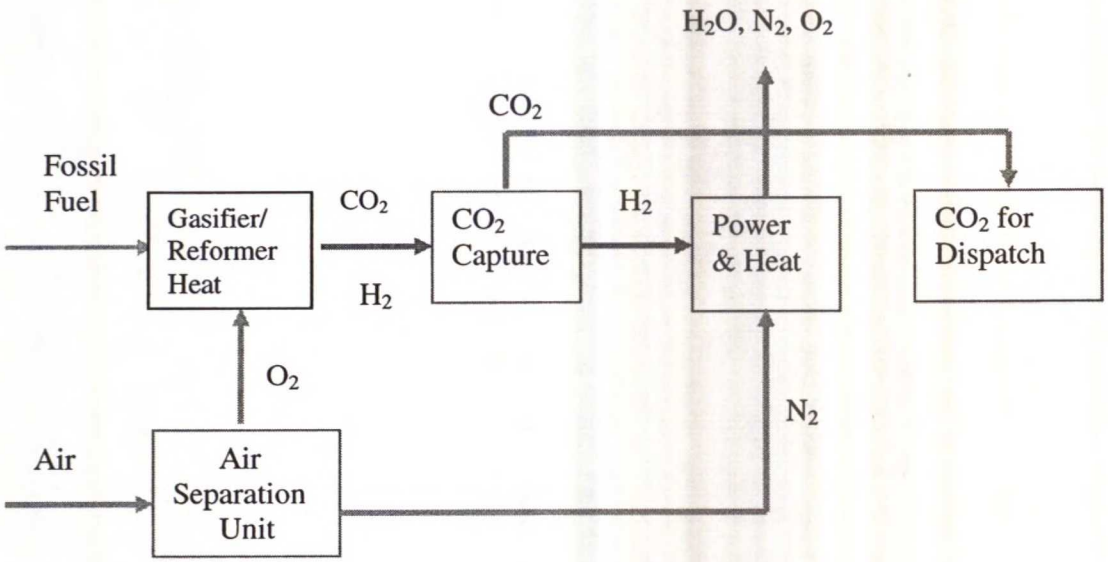

Fig. 3.2 Schematic diagram of the pre-combustion captures process.[16]

3.1.3 Oxyfuel combustion

Oxyfuel combustion involves burning fuel in an O_2-CO_2 mixture to produce a high concentration CO_2 flue gas. The oxygen is derived from an air separation unit and CO_2 is recirculated from flue gas to the combustor making the O_2-CO_2 mixture. The combustion in pure oxygen may cause too high flame temperature, and it is recommended to use mixed O_2-CO_2 gas. The process of oxyfuel combustion is shown in Figure 3.3.

The advantage of this combustion process is that it is effective with high CO_2 concentration gas streams at elevated pressure. On the other hand, it favours the great reduction of nitrogen oxides because the combustion takes place in a low-nitrogen environment. However, the disadvantage is that the air separation plant increases the cost and energy consumption. So far the operation of this option brings some uncertainties in the aspect of dealing with the corrosion, air entrainment, degree of flue gas clean up needed before CO_2 capture, and such questions have to be handled in the near future.[16]

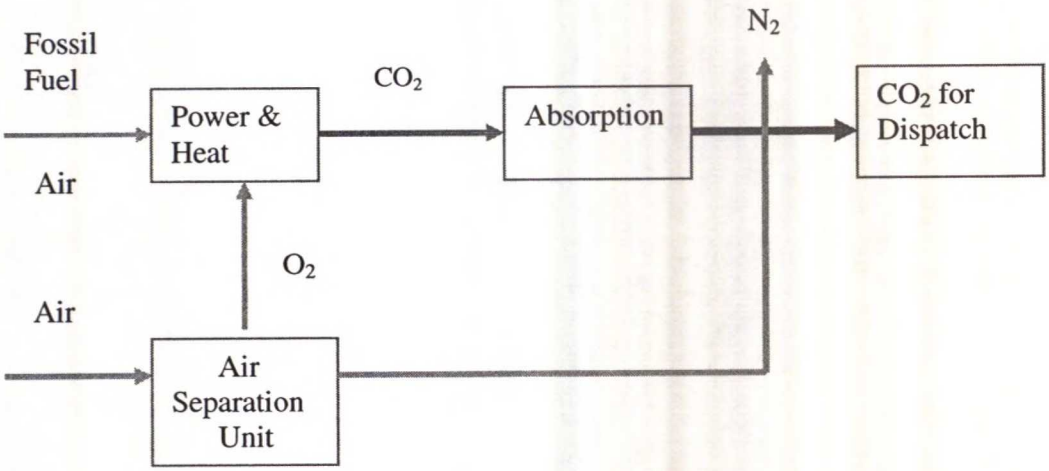

Fig. 3.3 Schematic diagram of the oxyfuel combustion capture process.[16]

3.2 CO_2 capture technologies

All above three CO_2 capture processes involve the separation of CO_2 from a gas stream, in generally, four technologies considered are identified. These include solvent scrubbing; physical and chemical adsorption, cryogenics and membrane separation.[13] An important aspect of CO_2 capture technologies is the extra amount of energy required by existing systems, which reduce the overall efficiency of generation. The major limitation of using such technologies is the high cost of separating CO_2 from flue gases. The cost of capturing CO_2 varies with plant type, being greater for gas-fired plant than for a coal-fired plant. Radical approaches to capture or to combustion of fossil fuels are required in order to reduce these costs

substantially. It is uncertain whether this can be achieved through improvement to the separation process alone, an alternative process of generation and capture could be also considered.[1]

3.2.1 Solvent scrubbing

The amine scrubbing technology is well established for removal of hydrogen sulphide and CO_2 from exhaust gases in the oil and chemical industries. Two types of scrubbing technologies are involved, chemisorption and physisorption. Chemisorption is based on the use of alkanoamine, such as chemical solvent, monoethanolamine (MEA) or diethanolamine (DEA). Typically, in CO_2 removal stage, the amine solvent selectively absorbs the CO_2 by chemically reacting with it to form a loosely bound compound. The CO_2 –rich absorbent is then pumped into a stripper tower where the pressure is reduced and meanwhile the temperature is increased to about 120 °C, CO_2 is released and then compressed. The regenerated absorbent is recycled to the stripper in a fully continuous process, which can achieve a CO_2 recovery rate of up to 98 %, with a purity of 99 % by using MEA solvent. Recently, more advanced amines, for example, N-methyldiethanolamine (MDEA) and 2-amino-2-methyl-1-propanol (AMP) have been developed and widely applied. The priority of MDEA is its efficiencies when the absorber is operated at high solvent loading and short contact times.

For over 60 years, physical absorption and other processes have been used in the petroleum, natural gas, and chemical industries to remove acid gases such as hydrogen sulphide (H_2S) and CO_2 during natural gas sweetening and H_2 production. It is considered to be the preferred technique for applications at higher pressure. The physical solvents commonly used include cold methanol, which is used in Rectisol process; dimethylether of polyethylene glycol in Selexol process, and propylene carbonate in Fluor Solvent processes. Other absorbents include calcium oxide (CaO), sodium hydroxide (NaOH) and potassium hydroxide (KOH). In addition, hybrid solvents combine the best characteristic of chemical and physical solvents appropriate to the application. Typical hybrid solvents include Purison, sulfinol, A-MDEA and ucarsol.

However, scrubber-based systems are all characterised by corrosion in the presence of O_2, relatively high cost and low energy efficiencies, compared to what society is willing to pay for CO_2 emission mitigation. Improved solvent with higher CO_2 absorption capacities, low vapour pressure, high degradation resistance and low corrosives in the presence of O_2 are expected.[1, 16, 17, 18]

3.2.2 Adsorption

Capture of CO_2 by adsorption is the most effective method when the concentration in the gas is between 400 ppm and 15000 ppm in power stations.[10] Some solid materials with high surface area can be used to separate CO_2 from gas mixtures by adsorption. These include certain zeolites and activated carbon. Several techniques for CO_2 capture are utilised, such as, pressure swing adsorption (PSA), temperature swing adsorption (TSA), and electrical swing adsorption (ESA).

A typical PSA unit is composed of a series of vessels, each containing the same type of adsorbing media such as activated carbon. At elevated pressure and low temperature, the gas flows through a packed absorbent bed by the adsorption process until it reaches equilibrium conditions at the bed exit. After the adsorption bed is loaded, the feed gas is switched to a clean adsorption bed and the loaded adsorption bed is regenerated. Regeneration can be accomplished by depressurising the adsorbent bed and purging it with some of the plant's gas. CO_2 with other off gases from the regeneration process is compressed for transport and storage. The TSA technique has almost the same process except that regeneration occurs by raising its temperature. ESA uses a novel carbon-bonded activated carbon fibre as the adsorption medium, which is highly conductive. Adsorbed gases can then be rapidly desorbed via a low-voltage electrical current. Activation conditions for these adsorbents may be varied to increase or decrease pore size, pore volume, and surface area to make the carbon fibre a more effective CO_2 adsorbent.

Both PSA and TSA have been used in H_2 production, bulk separation of O_2, and in the removal of CO_2 from natural gas. ESA with its energy saving potential is not yet commercially available. The adsorption variables like temperature, partial pressures,

surface forces, and adsorbent pore sizes are critical as they define the limits of the capacity and selectivity. Therefore these methods are not yet attractive for large-scale separation of CO_2 from flue gas, and the energy required for regeneration is high. Therefore, adsorbents that can operate at higher temperatures in the presence of steam with increased capacity and improved selectivity are needed.[1, 16, 17, 18]

3.2.3 Membrane separation

Membranes can be used to separate gases by allowing selective and specific permeation under conditions appropriate to its function between gases and the membrane material. Two types of membrane systems with respect of CO_2 capture are considered: gas separation membranes (ceramic and polymeric) and gas absorption membranes.

Gas separation membranes are thin files that selectively transport gases through the membrane based on physical or chemical interactions between the gas mixture and the membrane. The separation of the gases works as a function of the solubility or diffusivity of the gas molecules in the membrane, the partial pressure differences between two sides of the membrane acts as the driving force for gas separation.

Gas absorption membranes are microporous solid materials that are used as contacting devices between a gas flow and a liquid flow. The CO_2 diffuses through the membrane and is removed selectively by the absorption of the liquid on the other side of the membrane. Membrane gas absorption is considered as cost – effective technique for CO_2 from flue gases.

Membrane systems are relatively simple modular systems, which don't contain large amount of associated hardware. They also require less energy for operation than other methods of capture. One system that showed promise was the combination of membranes with chemical solvents. The membrane technology for gas separation is still considered as a developing technology for CO_2 capture. The drawbacks of this separation method are that they cannot usually achieve high degrees of separation, so

multiple stages or recycling of one of the streams is necessary. For multiple gas mixtures, several membranes with different characteristics are required to separate and capture high-purity of CO_2. Additionally, membranes used for the large scale of gas separation required for CO_2 capture from power plant flue gases haven't been very promising.[1, 19, 20]

3.2.4 Cryogenic separation

Cryogenic separation is used to liquefy and purify CO_2 from streams that have a high percentage of CO_2 (more than 90 %). The process is normally operated at low temperatures (below 0 °C) and using both pressure and temperature control. Particulate matter and other contaminants are also removed in the process. The main principle of cryogenic separation is to use different condensation temperatures of gases. When CO_2 is cooled below its boiling point, it begins to condense into a liquid state. Other gases from the mixture will liquefy in different temperatures. They will then be separated into pure components.

Cryogenic processes could be achieved in future Integrated Gasification Combined Cycle (IGCC) plants designs since it is only considered for high concentration of CO_2 flue gas applications. The cryogenic separation technique has the advantage that it does not add water and chemicals to the flue gas stream. The main disadvantage of cryogenic separation is that the process is most cost effective for gas streams with high concentration of CO_2 and can significantly decrease net plant efficiency when applied to streams with low CO_2 concentration. The development of efficient refrigeration may enable cryogenic separation to be less energy intensive and more competitive.[1,20]

3.3 CO_2 storage

Once CO_2 has been captured, it can be stored or utilized in order to prevent emissions from reaching the atmosphere. Carbon dioxide storage options are more dependent on geographical location, but largely independent of the type of power plant and capture technology employed. The options considered are: storage in depleted oil and gas

reservoirs, in deep unminable coal beds, in deep saline aquifers, ocean storage and terrestrial storage as a solid.[1, 14, 21]

3.3.1 Deep saline aquifers

Deep saline aquifers is a technique for sequestration of large amounts of CO_2, and it contains the largest potential capacity for storage among all the geological options. They are widely distributed below the continents and the ocean floor, and easy to access a number of power plants. Aquifers are typically formed in carbonate or sandstone formations, their pore structure and low permeability are considered suitable for CO_2 storage. When CO_2 is injected into water filled saline aquifer, it displaces the water without mixing together to form a single fluid phase. Some of the CO_2 dissolves in water, and the rate is dependent on the size and shape of the gas-water interface. [1, 16, 22, 23]

There are two basic types of deep saline aquifers, open and closed. Closed aquifers are preferred for onshore storage, because they have defined boundaries produced by geological folding or faulting, which considerably reduces the possibility for lateral movement and slow seepage of CO_2 into potable aquifers or to the surface. Comparing with closed aquifers, open aquifers are flat or gently sloping formations of water bearing rack. CO_2 can move laterally, and the rate of transport is rather slow, but their capacity is greater than closed aquifers.[16] Storage of CO_2 into deep saline aquifers should be geostructurally secure, otherwise, CO_2 could leak to shallow groundwater aquifers and brings detrimental effects on the water quality of potable aquifers. It is suggested that at depths greater than about 800 m, the stored CO_2 may be held in a supercritical state under a pressure with a minimum value of 7.4 MPa, and temperature with 31.1 °C, for at least hundreds or thousands years. [22]

In 1996, the world's first commercial-scale storage of CO_2 in aquifer was begun by Statoil in the North Sea Sleipner. Deep aquifer sequestration has proven to be technically feasible, and globally it could hold hundred years of CO_2 emissions.[14]

3.3.2 Oil and gas reservoirs

Oil and gas reservoirs consist of porous rocks covered by impermeable cap rock. They can be used as effective underground storage sites for CO_2. In enhanced oil recovery operation (EOR), CO_2 is injected into depleted oil reservoirs to increase the mobility of the oil and thus productivity of the reservoir. While most of the injected CO_2 remains in the reservoir, the CO_2 that comes along with the oil will be separated, recompressed, and injected back into the reservoir. The current reservoir engineering design is seeking the approach to minimize the total amount of CO_2 required to recover each barrel of oil.[1]

EOR process is technically feasible for oil, utility and coal companies. In order to improve the economics of CO_2 captured from power plants for EOR, the power plant should be located near the EOR operation. Currently most of the CO_2 used for EOR comes from natural CO_2 reservoirs. [1, 24]

Depleted natural gas fields are also feasible sites for CO_2 storage. Underground storage in natural reservoirs has been utilized in natural gas industry for many decades. Unlike oil reservoirs, CO_2 is not currently used to enhance the recovery of natural gas. An advantage of depleted natural gas fields is that they are in integral component of natural gas pipeline delivery systems, which can improve the economics of CO_2 transport and sequestration.[1]

Recent research has showed that there is enough capacity to store CO_2 underground in depleted oil and gas reservoir for hundreds of years. The high cost brings some question marks on performing this on large scale. Comparing the cost of generating electricity with coal and storing the carbon underground, it is only about 14 % as that of solar-powered electricity. It brings remarkable potential for countries like China and India, both which are utilizing huge quantities of coal. Today there is only 0,01 GtC/year of carbon as CO_2 is injected for enhanced oil recovery, in the next 50 years, it will require 100 times of this techniques in storaging CO_2.[14]

3.3.3 Unmineable coal seams

Unmineable coal seams offer another potential geologic storage medium for CO_2. CO_2 is injected into suitable coal seams, where it will be adsorbed by the coal, displacing previously adsorbed methane. Injection of CO_2 enables more methane to be extracted, while at the same time sequestering CO_2. The methane absorbed in the coal desorbs, diffuses, and flows with the water to the production well. [1, 14]

Coal seams must be saturated with gas, located at suitable depths and in simple structures, and also have sufficient permeability properties. Other factors that impact production include the quality and concentration of the gas as well as porosity of the coal. Coal in NW Europe has relatively low permeability, which makes the process harder. This problem can be addressed by hydro-fracturing, which injects water and sand at high pressure.

Unmineable coal seams technology is widely practised in the U.S. and to some extent elsewhere. From a global point of view, the capacity of CO_2 storage by deep unminable coal seams was estimated in 1990, it will only accept less than 2 % of CO_2 emissions by 2050, and it will not have a significant impact. Hence, some technique improvements with respect of verifying the capability, stability and permanence of CO_2 storage in coal-bed reservoir intervals are needed. Improved injection engineering and design techniques to optimise CO_2 sequestration and methane production should be also developed. Innovations in drilling techniques are implemented to cut down the high cost of drilling.[1, 16, 23]

3.3.4 Ocean storage

The exchange of carbon between the surface and deeper layers of ocean is accomplished through transport by water motions. Even though the oceans are the natural sink and have long-term potential in storing large quantities of CO_2, the resulting acidic condition will have an effect on ocean ecosystem. Two options at this moment are discussed for ocean storage: direct CO_2 injection and indirect sequestration.[1, 4, 14]

Direct injection of CO_2 into the deep ocean would be applied to large single sources of CO_2, such as a coal-fired power station. Different form of CO_2 is transported to deep sea by tanker or by pipelines based on various depths. Typically, in depths shallower than 450 meters, CO_2 is injected as gas bubbles, and below that depth, it is injected as liquid. CO_2 is highly soluble in the cold, dense water, and water temperatures decreases dramatically with depth. Below a sea level of 3700 meters, liquid CO_2 becomes dense enough that it sinks to the sea floor and forms a stable CO_2 "lake". [26] Globally, there is only 7 % of the total anthropogenic CO_2 is found at a depth of over 1500 m. [25] However, direct CO_2 injection might not be a suitable option to perform, because it has potentially dangerous environmental effects. The environmental impact on benthic life forms of the bathypelagic, abyssopelagic and hadopelagic zones are still unknown.[3]

Indirect sequestration is done through the enhancement of CO_2 uptake from the atmosphere by using fertilisation. Phytoplankton from photosynthesis present in surface water is consumed by larger plants, which are again consumed by other marine life forms like fish. It is so called "biological pump" where 70 to 80 percent of the fixed carbon is recycled to surface water, and the remaining organic matter will sink to the ocean floor as sediment where it is converted to CO_2 by bacteria. This process can be enhanced by using fertiliser, e.g. iron into regions that exhibit low phytoplankton levels.[26]

Global survey [25] has studied the oceanic anthropogenic CO_2 sink in 1994, it found that the taken CO_2 is not distributed evenly, North Atlantic stores 23 % of the global oceanic anthropogenic CO_2, although it only accounts for 15 % of the global ocean area; the Southern Ocean south of 50 °S takes only 9 % of anthropogenic CO_2; and more than 40 % of the anthropogenic CO_2 is stored in the region between 50 °S and 14 °S due to the fact of large area of ocean.

Since dissolving CO_2 in seawater will form protons bicarbonate and carbonate ions, and they decrease the pH of the water. In buffered seawater system the pH change is

small due to the dissolved carbon dioxide. The changes in the pH and speciation could still have unknown effect on the marine life. Ocean fertilization would aim to increase production of biological material in the oceans, drawing-down additional CO_2 from the atmosphere. In considering this concept as a potential sequestration option, it is recognized that the 'biological pump' would transfer more carbon from the surface layers to deep water. Most of this organic carbon would be re-mineralized to inorganic carbon; much of the nutrients should also be recycled, and so be available for further biological production. [1,4]

3.3.5 Other options

While CO_2 sequestration in terrestrial ecosystems poses no health, safety or environmental threats and, in fact, improves land and water quality, its capacity is limited. But the land areas required are huge (for example, about 2000 km^2 would be required to absorb the CO_2 produced in a lifetime of a 500 MW coal-fired power station). Uncertainties about land availability, elasticity of price and security of CO_2 storage raise questions.

The most important processes in the exchange of carbon are photosynthesis, autotrophic respiration (i.e., CO_2 production by the plants) and heterotrophic (i.e., essentially microbial) respiration converting the organic material back into CO_2 mainly in soils. The carbon balance can be changed considerably by the direct impact of human activities (land use changes, particularly deforestation), burning of coal, oil or gases, and by other changes in the environment, e.g., atmospheric composition. Since the pools and fluxes are large, any perturbation can have a significant effect on the atmospheric concentration of CO_2. But the disadvantage of photosynthesis process is that it is climate dependent, e.g. it only works a few hours in the daytime. [1, 4, 21, 27]

3.4 Utilisation of CO_2

CO_2 is already used for a wide range of purposes. These include using CO_2 as a feedstock for manufacture of chemical products, enhancement of the production of crude oil, and in growth of plants or algae (for use as a bio-fuel). Utilization may help

to remove CO_2 from the environment and can make a contribution to reduce the emission problems.[18]

3.4.1 Chemicals manufactured from CO_2

The catalytic reduction of CO_2 by alkanes is well known with those based on the Mobil HZSM-5 series of catalysts being particularly effective. The reactions are:

$$CO_2 + C_3H_8 \rightarrow CO + C_3H_6 + H_2O \text{ (metal oxide based catalysts)} \quad (3.1)$$

$$CO_2 + C_3H_8 \rightarrow CO + \text{aromatics} + H_2O \text{ (Zeolite based catalysts)} \quad (3.2)$$

The reaction yield in producing aromatics (BTX Benzene, Toluene and Xylene) over ZSM-5 and similar catalysts could be increased by the addition of CO_2 to the alkane feed. The optimum temperature of reaction is 550 °C and yield and selectivity drop off at 600 °C. The use of CO_2 for this type of reaction scheme is limited by the demand for BTX and for the methanol by-product. Any "waste" CO_2 and propane are recycled and methanol could be recycled over alumina and then HZSM-5 to produce more BTX.[1] Since CO is the most toxic substance and it has to be removed, one way is to convert CO to CO_2 by addition of oxygen.[28]

The oxidative coupling of methane with CO_2 is a reverse water gas shift reaction and it produces synthesis gas hydrogen and carbon monoxide. Since both CO_2 and CH_4 are greenhouse gases, this reaction brings great attraction from both environmental and industrial perspectives. Most of the group VIII metals act as suitable catalysts, e.g. 1 wt% Cu and 8 wt% Ni/SO_2 catalyst has excellent long-term stability for this reaction at temperature higher than 760 °C, it brings over 90 % selectivity to produce synthesis gases.[29]

CO_2 can be also taken as a useful monomer to form alkylene oxides and alkylene poly-carbonates. The reaction normally involves an organometallic such as diethylzinc together with a hydrogen donor in the form of water, an amine or an aromatic dicarboxcylic acid. These are currently used as binders in the electronics

industry and are being further developed for film applications in the food and medical areas. [1]

Utilisation of captured CO_2 as a feedstock for production of chemicals is an attractive concept as long as the additional energy required is small; however, this is a tough target to meet since carbon dioxide is thermodynamically stable and so any use of CO_2 as a feedstock requires a significant amount of energy input.[1]

3.4.2 Enhanced oil recovery

With great capacity for storing CO_2 with enhanced oil recovery (EOR), it has great potential to employ on large scale in the future.[14] Carbon dioxide injected into depleted oil reservoir with suitable characterizers can achieve enhanced oil recovery by two processes, miscible or immiscible displacement. Miscible CO_2 displacement is that CO_2 is injected under a reservoir pressure (deeper than 1,200 meters) and oil density lighter than 22 ° API gravity, and mix with oil in the reservoir, the interfacial tension between the two substances disappears. Immiscible CO_2 displacement occurs when reservoir pressure is too low, or oil density is too dense, the injected CO_2 remains physically distinct from the oil in the reservoir. Miscible processes are more efficient than that of immiscible process. However, in immiscible process, the injected CO_2 can improve oil recovery by causing the oil to swell, reducing oil's density and thus improve its mobility.[1, 27]

3.4.3 Indirect biofixation of CO_2

The world's forests currently hold 90 % (740 Gt) of the ground terrestrial carbon, and forestry is the most commonly considered route for offsetting fossil-fuel CO_2 emissions by planting forests as indirect biofixation.

The CO_2 sequestration in long-term forest plantations differs between industrialized countries and developing countries. The developing countries with significant forestry potential are mainly tropical countries and only reforestation is considered. In the industrialised countries the plantations would mainly make use of excess pasture and low-producing arable land. A proportion of pasture and arable land in the

industrialised countries is considered to be available for forestation. Short rotation cropping involves the plantation of fast growing trees, which are harvested every 3-10 years and which retain the same root system for several generations. This would provide woodchip fuel for power generators. [1, 30]

3.4.4 Direct biofixation of CO_2

Direct biofixation of CO_2 is microalgae-based processes which can directly utilise high concentration of CO_2 from power station flue gas streams, therefore reduce CO_2 emissions from power plant. Terrestrial plants require near atmospheric concentrations of CO_2 for biomass production, and the growth of aquatic plants is restricted by the low rate of transport of CO_2 from the atmosphere to the oceans, in particular the productivity of microalgae is dramatically increased by artificially increasing transfer rate of CO_2 to the aqueous environment.

The mechanism of microalgae-based reaction is that, microalgae and cyanobacteria are groups of micro-organism, which have the capability for photosynthesis using water as the reducing agent:

$$CO_2 + H_2O \rightarrow CH_2O + O_2\,(g) \qquad (3.3)$$

The CO_2 fixation is catalysed by the enzyme RuBisCO which is bi-functional and it also catalyses the reverse reaction of photorespiration, which reduces the net efficiency of photosynthesis.

The location of power plant might restrict the direct use to grow algae in order to make bio-fuels. Artificial biomass schemes based on production of algae are uncompetitive at present but potentially offer high rates of take-up of carbon. [1, 4, 30]

4. THERMODYNAMICS OF SOME CO_2 SYSTEMS

4.1. Chemistry and thermodynamics of VLE systems

4.1.1 VLE theory

Vapour/liquid equilibrium (VLE) is the state of coexistence of liquid and vapour phases. Raoult's law and Henry's Law define ideal system and ideal dilute solution.

Raoult's law is

$$y_i P = x_i P_i^* \quad (i = 1, 2, \ldots N) \tag{4.1}$$

where x_i is a liquid-phase mole fraction, y_i is a vapour-phase mole fraction, and P_i^* is the vapour pressure of pure species i at the temperature of the system. The product $y_i P$ on the left side is partial pressure of species i.

For low to moderate pressures where an ideal gas phase and real liquid phase exist, the reality in the liquid phase is expressed through the activities a_i that shows deviation in the liquid phase from Raoult's law

$$y_i P = x_i \gamma_i P_i^* \quad (i = 1, 2, \ldots, N) \tag{4.2}$$

where

$$a_i = x_i \gamma_i \tag{4.3}$$

The factor γ_i is the activity coefficient, and a_i is the activity of the component.[31]

Henry's Law states that the partial pressure of the species in the vapour phase is linearly proportional to its liquid-phase mole fraction,

$$y_i P = x_i H_i \tag{4.4}$$

where H_i is Henry's constant. Henry's law is valid for any species present at low concentration, but as mentioned is limited to systems at low to moderate pressures.

4.1.2 Solubility of gases in liquids

The solubility of a gas in a liquid is an example of vapor-liquid phase equilibrium. When the system is in mechanical, thermal and chemical equilibrium, then:

$$T^{V} = T^{L} \tag{4.5}$$

$$P^{V} = P^{L} \tag{4.6}$$

$$\mu_i^{V} = \mu_i^{L} \tag{4.7}$$

And the fugacities, f_i, of the components are equal between the two phases

$$f_i^{V}(T, P, y_i) = f_i^{L}(T, P, x_i) \tag{4.8}$$

There are for species i in real phases,

$$\phi_i \equiv f_i^{V} / y_i P \tag{4.9}$$

$$f_i^{L} \equiv x_i \gamma_i f^{\circ}{}_i^{L} \tag{4.10}$$

where ϕ_i is the fugacity coefficient of species in gas phase and y_i the mole fraction of gaseous species.[31,32] Putting into equation (4.8), the vapor-phase fugacity coefficient, ϕ_i, and the liquid-phase activity coefficient, γ_i, gives

$$y_i \phi_i(T, P, y) P = x_i \gamma_i(T, P, x) f_i^{oL}(T, P) \tag{4.11}$$

where $f^{\circ}{}_i^{L}(T, P)$ is an appropriate standard-state fugacity for the liquid phase.

Chemical potential for gas and liquid phase are derived as follows:

$$\mu_i^V(T, P, y_i) = \mu_i^{oV}(T) + RTln(P/P^0) + RTlny_i + RTln\phi_i$$
$$= \mu_i^{oV}(T) + RTln(y_i P\phi_i/P^0) \quad (4.12)$$

$$\mu_i^L(T, P, x_i) = \mu_i^{\phi L}(T, P) + RTlnx_i + RTln\gamma i = \mu_i^{\phi L}(T, P) + RTlna_i \quad (4.13)$$

where $\mu_i^{oV}(T)$ and $\mu_i^{\phi L}(T, P)$ the standard chemical potentials.[32,33]

4.2. The solubility of CO_2 in water

Carbon dioxide is one of the most important volatile weak electrolytes in industry. The solubility of CO_2 in water occurs according to the physical equilibrium[6]:

$$CO_2\,(g) = CO_2\,(aq) \quad (4.14)$$

And the chemical equilibrium:[7]

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+ \quad (4.15)$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \quad (4.16)$$

Figure 4.1 shows the chemical equilibrium of CO_2 in a closed system. The equilibrium between the vapour phase and the liquid phase for equation (4.14) in Henry's law scale is given as follows:[34]

$$y_i\phi_i P = m_i\gamma_i H_{ij} \quad (4.17)$$

where m_i is the molality of CO_2 (mol/kg H_2O).

At very low concentrations, the equilibrium between gas phase and liquid phase is determined primarily by Henry's constant H and the molality of molecular solute. Since ions are not volatile, the phase equilibrium of the system is governed not by the total electrolyte concentration in the liquid, but only by that concentration of liquid phase electrolyte, which exists in molecular (undissociated) form. The un-dissociated CO_2 is in chemical equilibrium with its dissociation products bicarbonate and carbonate anions and protons.[34] In a aqueous solution the non-dissociated CO_2(aq) is in chemical equilibrium with its dissociated species bicarbonate and carbonate.

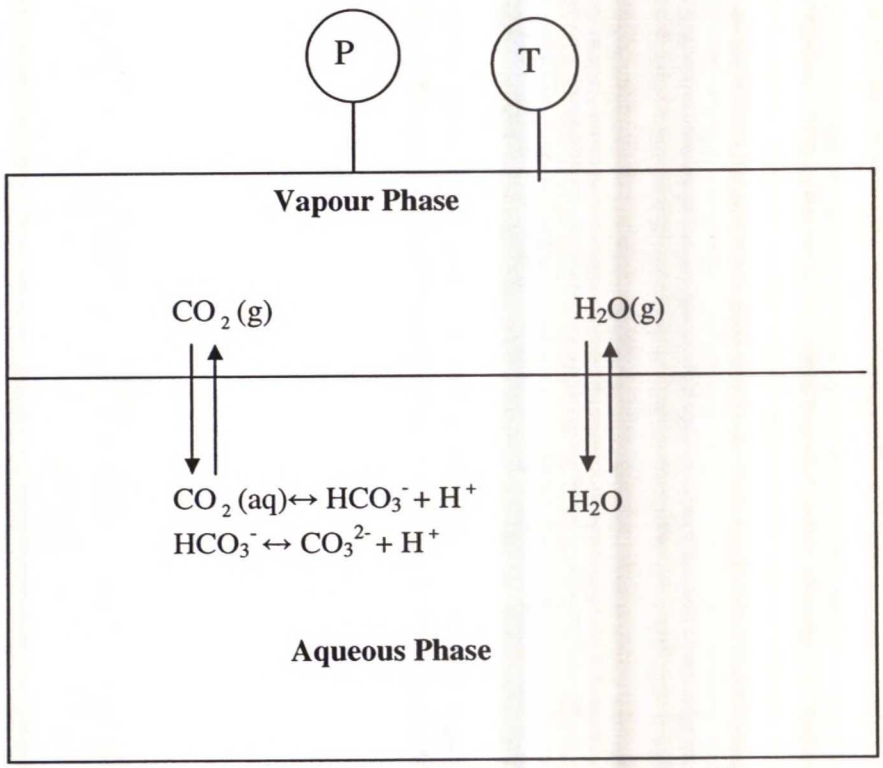

Fig. 4.1 Vapor-liquid equilibrium in a single-solute system.[7,34]

The model of Carroll et al.[9] is based on Henry' law and was used to correlate the low pressure data up to 1 MPa, it neglects liquid phase non-idealities. The correlation is valid in the range from 0 °C to 160 °C. It describes Henry's constant for CO_2 as:

$$\ln(H_{CO_2}/\text{MPa})$$
$$= -6.8346 + 1.2817\cdot10^{4}(\text{K}/T) - 3.7668\cdot10^{6}(\text{K}^2/T^2) + 2.997\cdot10^{8}(\text{K}^3/T^3) \quad (4.18)$$

The effect of temperatures on the solubility of CO_2 in water is shown in Figure 4.2. The curve shown was calculated using the model of Carroll et al,[9] experimental values from Zawisza et al.,[35] and Kiepe et al.[36] are also included. In general, the experimental data are in good agreement with the model. Henry's law can be applied for the solubility of a gas in a liquid. It states that the partial pressure of a gas in equilibrium with a liquid is proportional to the concentration of the gas in the liquid. That is [37]

$$p_{CO_2} = H_{CO_2-H_2O} x_{CO_2} \quad (4.19)$$

where $H_{CO_2-H_2O}$ is Henry's constant with unit bar or MPa.

At constant pressure, Henry's constant increases with the temperatures until a maximum value 586 MPa is reached at 150 °C.

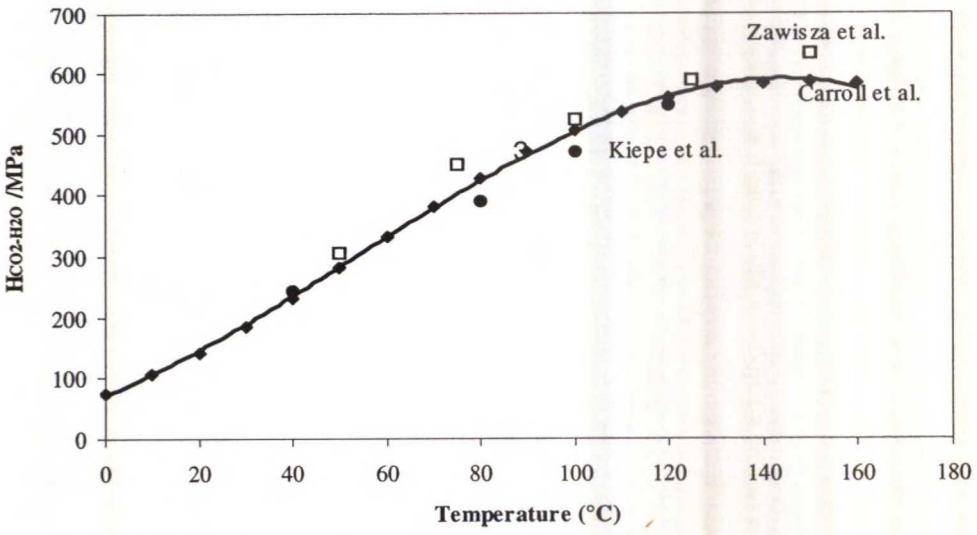

Fig. 4.2 Henry's constant for CO_2 solubility in water as a function of temperature: (◆) Carroll et al.[9] (□) Zawisza et al.[35] (•) Kiepe et al.[36]

The effect of pressure on the solubility of CO_2 as a function of mole fraction of CO_2 at different temperatures is observed in Figure 4.3 [36]

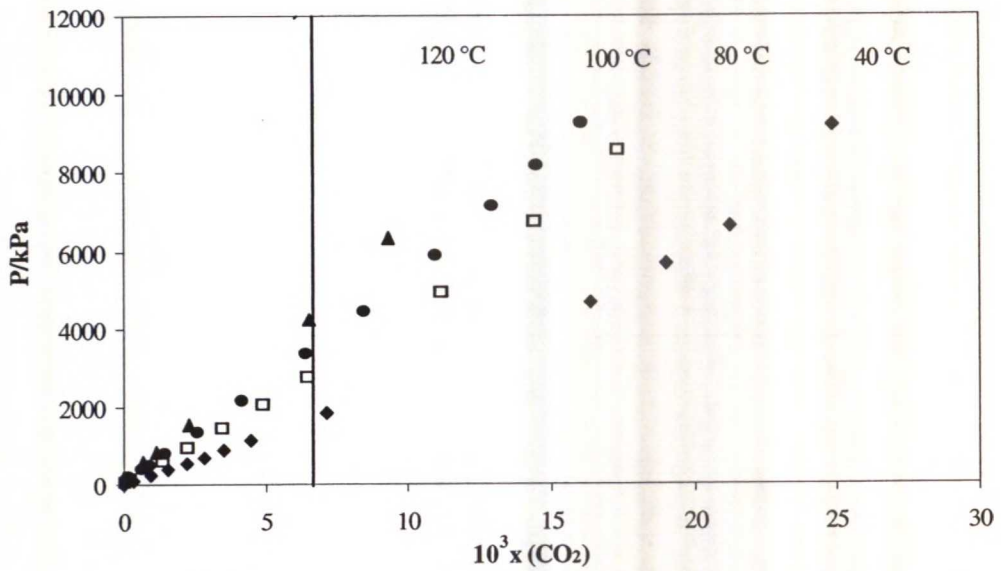

Fig. 4.3 The solubility of carbon dioxide in water as a function of pressure and temperature: (◆) 40 °C; (□) 80 °C; (●) 100 °C; (▲) 120 °C. [36]

At constant temperature, the partial pressure of CO_2 is increasing with the mole fraction of CO_2 in liquid phase.

4.3 The solubility of CO_2 in aqueous alkanolamine solutions

The removal of acid gases CO_2 and H_2S, by a liquid solvent is important in many industrial processes, such as natural or refinery gas processing and coal gasification. The most commonly used technology is absorption in alkanolamines, also known as acid gas sweetening. Monoethanolamine (MEA), N-methyldiethanolamine (MDEA), diethanolamine (DEA), and 2-Amino-2-methyl-1-propanol (AMP) are among the alkanolamines used in the process. The alkanoamines are named as primary, secondary, or tertiary, depending on the degree of the substitution of the central nitrogen. Monoethanolamine (MEA) is a primary amine and shows a single substitution on the central nitrogen. Diethanolamine (DEA) is a secondary amine and

shows a double substitution and N-methyldiethanolamine (MDEA) as a tertiary amine shows triple substitution. [38]

The basic flow sheet for the alkanolamine acid-gas absorption process systems is shown in Figure 4.4.

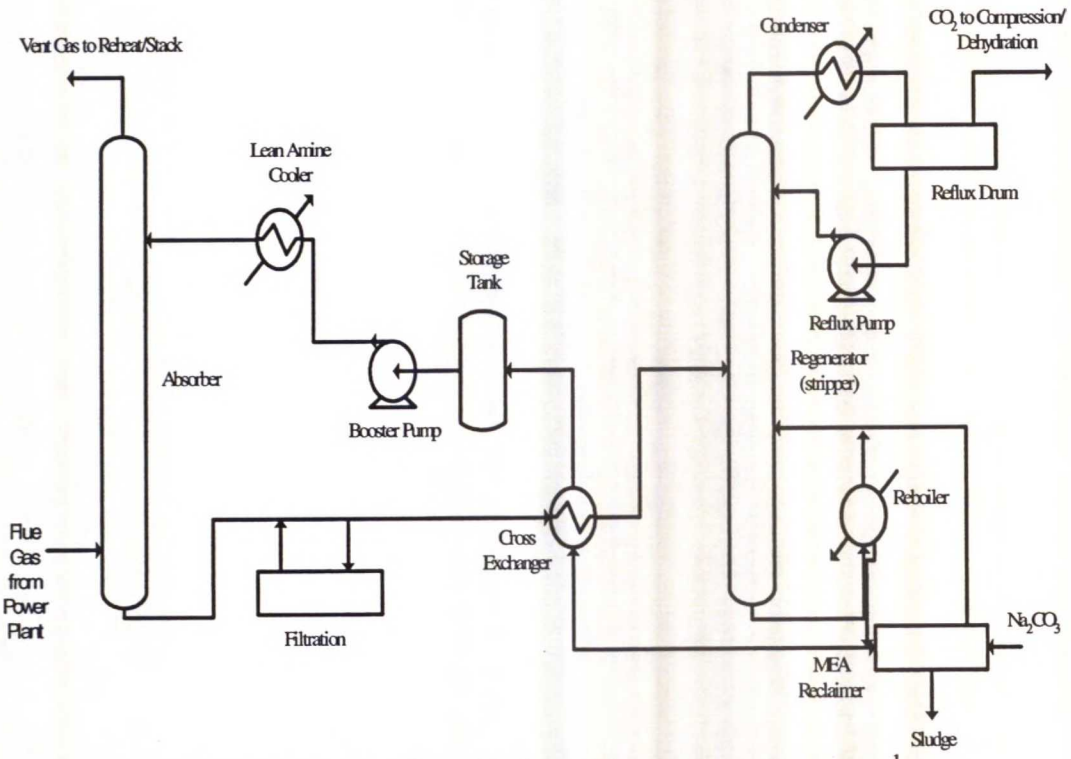

Fig. 4.4 Basic flow scheme for alkanolamine acid-gas removal process. [1]

Gas to be purified is passed upwards through the absorber, countercurrent to a stream of the solution. At the bottom of the absorber, rich solution is heated by heat exchange with lean solution from the bottom of the stripping column. It is then fed to the stripping column at some point near the top. Acid gas that is removed from the solution in the stripping column is cooled to condense a major portion of the water vapour. This condensate is continually fed back to the system in order to prevent the amine solution from becoming more concentrated. A major portion of water is fed back to the top of the stripping column and absorbs and returns amine vapours carried by the acid gas stream.

The absorption of CO_2 by alkanolamine solution happens mainly by chemical absorption, which means that CO_2 is reacting with the alkanolamines. The overall reactions are complex and their mechanism comprises a series of simple reactions. The rate determining step involved in primary and secondary amines reaction mechanism is the formation of carbamate ions as given by the following equation,

$$2RR'NH + CO_2 \leftrightarrow RR'NCOO^- + RR'NH_2^+ \quad (4.20)$$

where RR'NH represents an alkanolamine, $RR'NCOO^-$ is the carbamate, and $RR'NH_2^+$ is the protonated amine.

Both kinetic and thermodynamic equilibrium in this step determines the ultimate gas loading (mol of acid gas captured / mol of amine). Tertiary amine solutions cannot react directly with CO_2 to form carbamate.[38, 39]

Gas absorption with alkanolamines has problems such as foaming, thermal degradation of the alkanolamine solution, and corrosion of materials. To solve such limitations, effort has been placed on developing improved absorbents that contain higher amounts of anticorrosive and antifoaming agents.[40]

4.3.1 The solubility of CO_2 in aqueous MEA solution

Amines with two hydrogen atoms directly attached to a nitrogen atom are called primary amines like monoethanolamine (MEA). It is one of the most used primary alkanolamine for CO_2 absorption mainly due to its relatively low molecular weight, strong base properties, high reactivity, low solvent cost, ease of reclamation and low absorption of hydrocarbons. [38, 40, 41, 42] The main disadvantage of MEA solutions is that they are more corrosive than solutions of most other amines, particularly if the amine concentrations exceed 20 %. Corrosion inhibitors permit MEA concentrations as high as 30 % to be used but they are only effective in CO_2 removal systems, not proven to be reliable in preventing corrosion with CO_2 / H_2S mixtures. In addition the high heat of reaction of MEA with CO_2 and H_2S requires higher energy for stripping

systems than other amine solutions. Finally, the relative high vapor pressure of MEA causes significant vaporization losses, particularly at low-pressure operations.[38]

The reaction steps for the absorption of CO_2 are as follows: [43]

$$2RNH_2 + CO_2 + H_2O \leftrightarrow (RNH_3)_2CO_3 \quad (4.21)$$

$$(RNH_3)_2CO_3 + CO_2 + H_2O \leftrightarrow 2RNH_3HCO_3 \quad (4.22)$$

$$2RNH_2 + CO_2 \leftrightarrow RNHCOONH_3R \quad (4.23)$$

where R stands for the (CH_2CH_2OH) group.

The data obtained from the literature for CO_2 solubility in 15.3 wt % MEA in aqueous solution at 313.2 K are plotted in Figure 4.5. The partial pressures of carbon dioxide ranges from 1 to 3160 kPa.

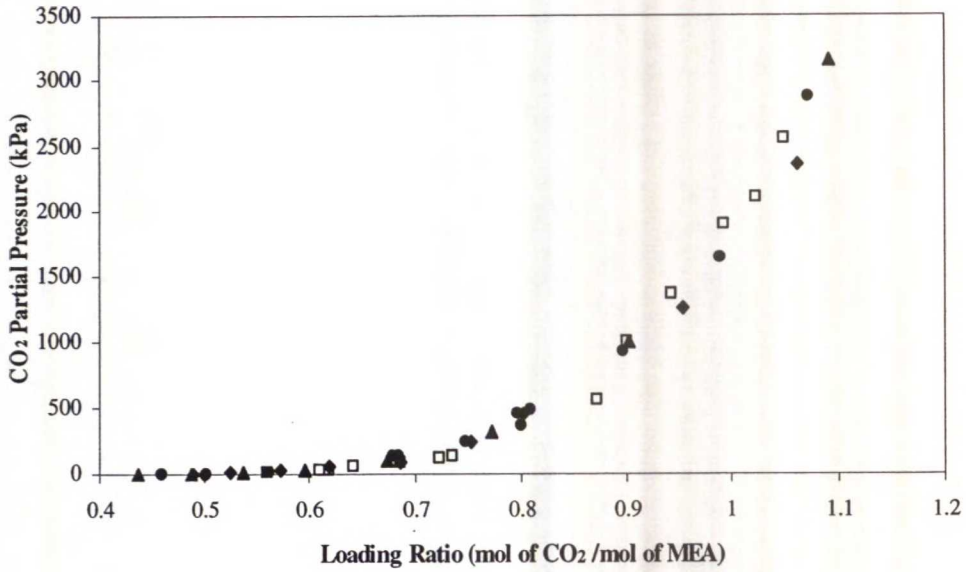

Fig. 4.5 Solubility of carbon dioxide in 15.3 wt % MEA aqueous solution at 313.2 K: (♦) Song and Lee [42] (□) Shen and Li [44] (▲) Lee et al.[41] (●) Lee et al.[45]

The comparison of the results in Figure 4.5 shows that they are in good agreement with each other at the low CO_2 pressures but deviates a little bit at higher CO_2 pressures. The higher the CO_2 partial pressure, the higher the CO_2 absorption capacity obtained in MEA aqueous solution. The equilibrium solubility of CO_2 in 30 wt % MEA at temperatures 40, 60, 80, 100 °C and at partial pressures of CO_2 varied between 1.1 and 1975 kPa as shown in Figure 4.6:[44]

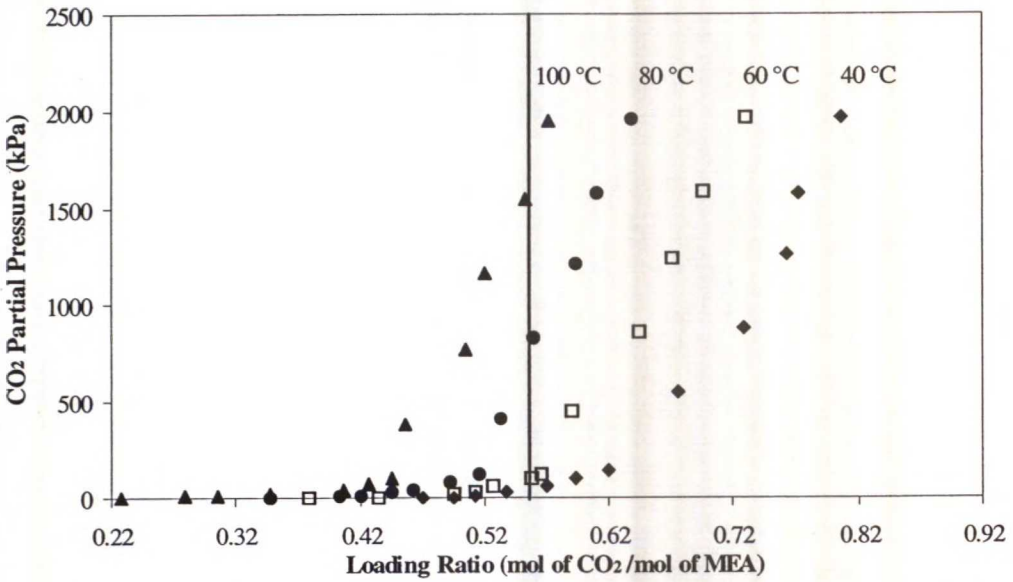

Fig. 4.6 Solubility of carbon dioxide in 30 wt % MEA aqueous solution at 40-100 °C: (◆) 40 °C; (□) 60 °C; (•) 80 °C; (▲) 100 °C.[44]

As can be seen in Figure 4.6, the solubility of CO_2 changes systematically with the temperature. At constant loading, pressure of CO_2 is increasing with the temperature shown by vertical line in the figure. Furthermore, at constant CO_2 partial pressure the CO_2 absorption capacity is higher at lower temperatures.

The effects of amine concentrations from 1 N to 5 N on CO_2 solubility is shown in Figure 4.7.[41] When loading is smaller than 0.7 mol of CO_2 / mol of MEA, the effect of MEA concentration on the solubility is very little; when the loading is above 0.7 mol of CO_2/mol of MEA, at a constant pressure the higher concentration of MEA solution corresponds to lower CO_2 solubility.

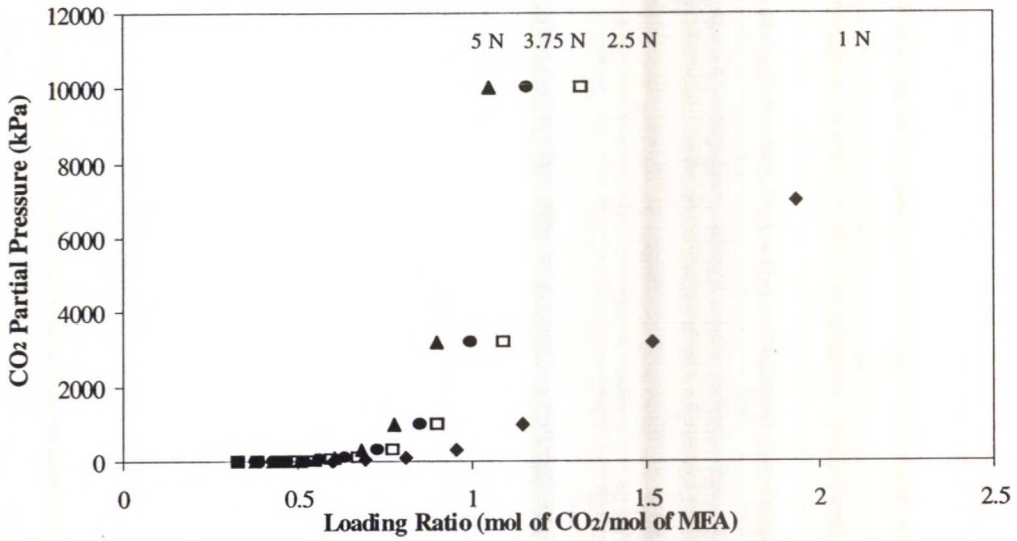

Fig. 4.7 Solubility of carbon dioxide at in different concentration of MEA aqueous solutions at 40 °C: (◆) 1 N; (□) 2.5 N; (●) 3.75 N; (▲) 5 N.[41]

4.3.2 The solubility of CO_2 in aqueous DEA solution

DEA have only one hydrogen atom directly attached to the nitrogen atom. Amines like DEA are called secondary amines.[38] Similar to MEA, DEA solutions are also extensively used for the removal of sour gases from natural gas and other hydrocarbon mixtures because of their high reactivity, easy regeneration, low hydrocarbon absorption, and low cost.[45] Compared to MEA, DEA is more thermally stable and has a lower enthalpy of reaction[38] and a lower volatility due to its low vapour pressure.[47, 48] In addition, DEA solutions are less corrosive than MEA solutions, since the acid gases are stripped easier requiring less vigorous reboiling.[49] One disadvantage of DEA solutions is that the reclaiming of contaminated solutions may require vacuum distillation.[38]

The reaction between CO_2 and DEA is reversible[50], the main reactions occurring in the system of CO_2 and DEA in aqueous solutions are as follows:[39]

Ionization of water:

$$H_2O \leftrightarrow OH^- + H^+ \quad (4.24)$$

Dissociation of carbon dioxide:

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+ \quad (4.25)$$

Dissociation of bicarbonate ion:

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \quad (4.26)$$

Protonization of DEA:

$$R_2NH + H^+ \leftrightarrow R_2NH_2^+ \quad (4.27)$$

Formation of carbamate:

$$R_2NH + HCO_3^- \leftrightarrow R_2NCOO^- + H_2O \quad (4.28)$$

where R represent (HOC_2H_4) group.

The influence of DEA concentrations on the equilibrium loadings at 100 °C is shown in Figure 4.8.[49] The partial pressure of CO_2 increases with CO_2 loadings. At a constant partial pressure, CO_2 solubilities decrease with increasing concentration of DEA.

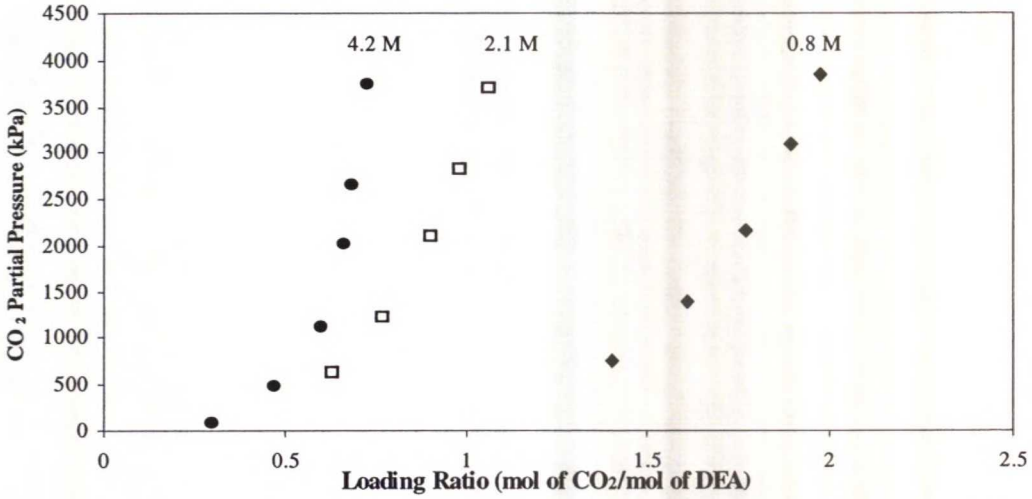

Fig. 4.8 Solubility of carbon dioxide in aqueous mixed solution of DEA at 100°C: (■) 0.8 M; (□) 2.1 M; (•) 4.2 M.[49]

Figure 4.9 shows the effects of temperature and pressure on the equilibrium CO_2 loadings. In general, the CO_2 absorption capacity increases with the pressure. When loading is grater than 0.4 mol of CO_2 / mol of DEA, a sharp increase of partial pressure of CO_2 can be observed. When partial pressure of CO_2 is constant, the higher the temperature, the lower is the CO_2 absorption capacity.

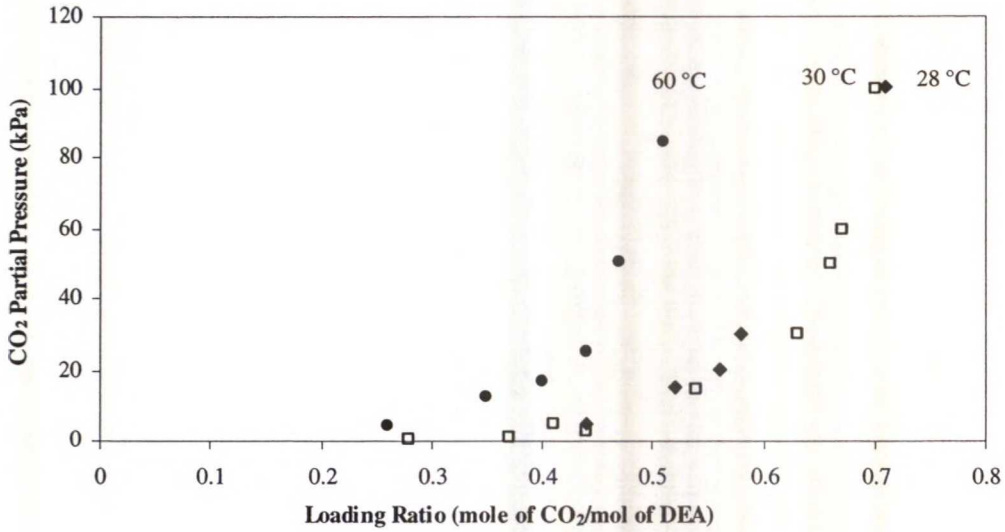

Fig. 4.9 Solubility of carbon dioxide in 2 M DEA aqueous solution at 28-60 °C: (◆) 28 °C; (□) 30 °C; (•) 60 °C.[52]

4.3.3 The solubility of CO_2 in aqueous MDEA solution

MDEA represent completely substituted ammonia molecules with no hydrogen atoms attached to the nitrogen, and is called tertiary amine. [38] As a result, MDEA cannot react directly with CO_2 to form carbonate, but needs the intervention of water. The reaction forms an intermediary zwitterion, and alkylcarbonates as a final product.

$$CO_2 + RR'R''N \leftrightarrow RR'R''N^+COO^- \quad (4.29)$$

$$RR'R''N^+COO^- + H_2O \leftrightarrow RR'R''NH^+ + HCO_3^- \quad (4.30)$$

The overall reaction can be regarded as the direct reaction of CO_2 with water in the presence of MDEA as a base catalysis,[53]

$$CO_2 + RR'R''N + H_2O \leftrightarrow RR'R''NH^+ + HCO_3^- \quad (4.31)$$

where R, R' and R'' represent (HOC_2H_4), (HOC_2H_4) and CH_3 groups, respectively.

The association of water with the tertiary amine MDEA molecules is critical since CO_2 doesn't react with MDEA in the absence of water.[54] Water molecules dissolve MDEA through hydrogen bonding, and this association allows MDEA to catalyze the hydration of CO_2.[55]

In the absorptive process, the stripping for the regeneration of the amine solution can easily be achieved by a simple pressure reduction due to the fact that MDEA does not directly react with CO_2. MDEA has favourable thermal and chemical stability, furthermore, MDEA shows low corrosive behaviour, and therefore, it can be employed at a high concentration in the absorbing process. Compared to conventional absorbents, the use of high concentration MDEA solutions brings significant electricity savings because of lower circulation demands in the absorption process. Since MDEA has a low vapour pressure, it leads to almost no evaporative loss during operation of the absorptive process. The reaction rate of MDEA with CO_2 is in

general very slow. By enhancing the physiochemical properties with specific MDEA additives can improve the absorbent's reactivity with CO_2.[54]

The solubility of CO_2 at fixed 5 wt % MDEA solution in different temperatures is shown in Figure 4.10. The solubility of CO_2 in MDEA solution decreases with the increasing temperatures at constant partial pressure. [56]

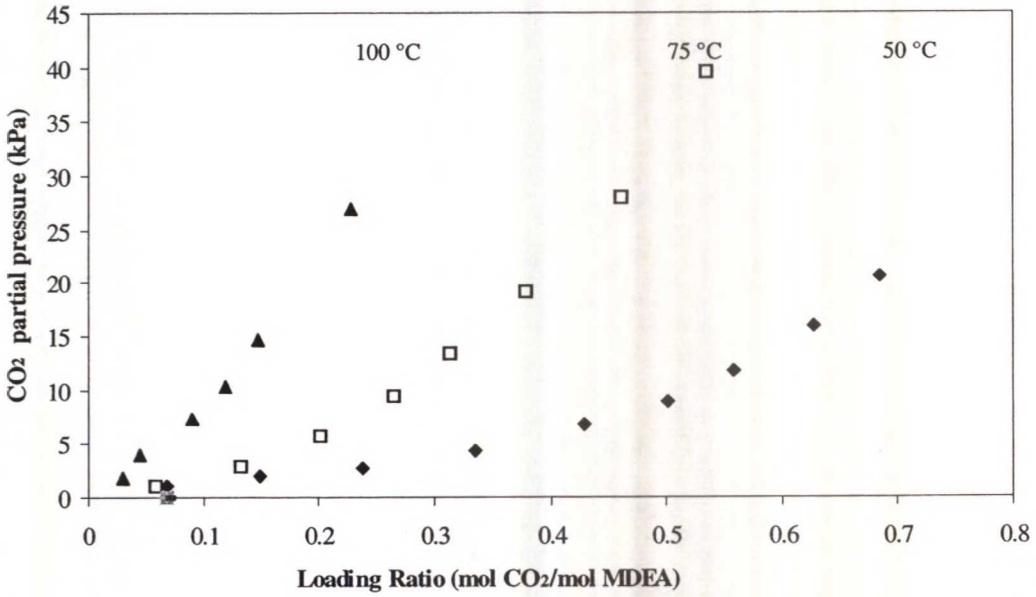

Fig. 4.10 Solubility of carbon dioxide in 5 wt % MDEA aqueous solution in different temperatures: (◆) 50 °C; (□) 75 °C; (▲) 100 °C. [56]

To illustrate the effect of MDEA concentration on its CO_2 absorption capacity at constant temperature, the absorption equilibria of CO_2 in MDEA solutions were plotted in Figure 4.11.[56]

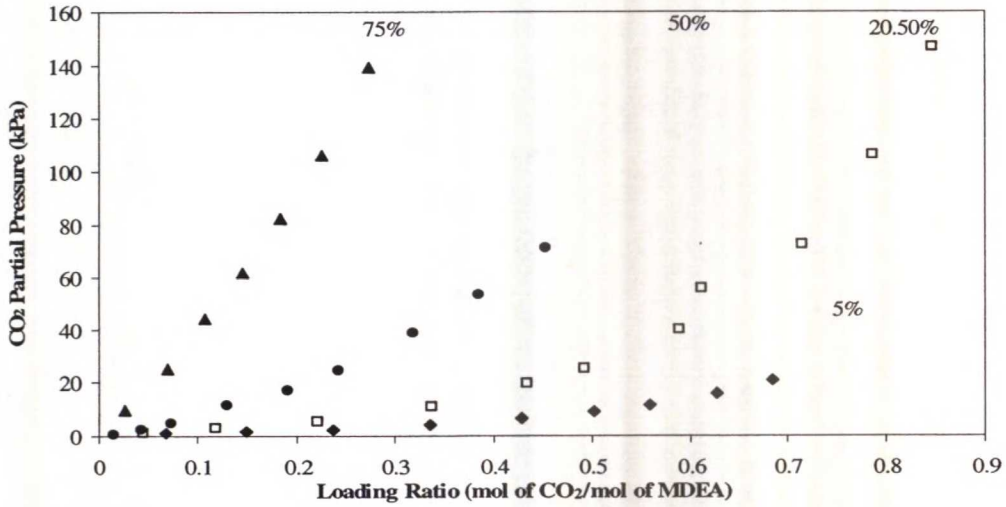

Fig. 4.11 Equilibrium solubility of carbon dioxide in MDEA solutions at 50 °C: (♦)5 wt %; (□) 20.5 wt %; (•) 50 wt %; (▲) 75 wt %.[56]

At a constant temperature the solubility of CO_2 changes with the concentration of MDEA solution significantly. For example, L = 0.25 mol of CO_2 /mol of MDEA, when 5 wt %, P =3.04 kPa; 20.5 wt %, P = 8.55 kPa; 50 wt %, P = 26.15 kPa; 75 wt %, P =123.16 kPa. The higher concentration of MDEA solution results increase in CO_2 partial pressure. Thus, it can be concluded that MDEA needs to be maintained at low concentration in order to increase the absorption capacity of CO_2 in aqueous MDEA solution.[56]

Methanol is widely used as a physical solvent for the removal of CO_2 from gas streams. Enhancement of the solubility of CO_2 in a mixture of MDEA by using methanol at constant temperature and pressure is industrially interesting. The solubility of CO_2 in an aqueous mixed solvent of 40 wt % MDEA and 40 wt % methanol, and a mixture of 48.7 wt % MDEA and 51.3 wt % water at 40 °C are compared in Figure 4.12.[49, 50] At higher CO_2 partial pressures (loading is greater than 1 mol CO_2 / mol MDEA), the solubility of CO_2 in the aqueous mixed MDEA-methanol system becomes significantly greater than in the aqueous MDEA solution.

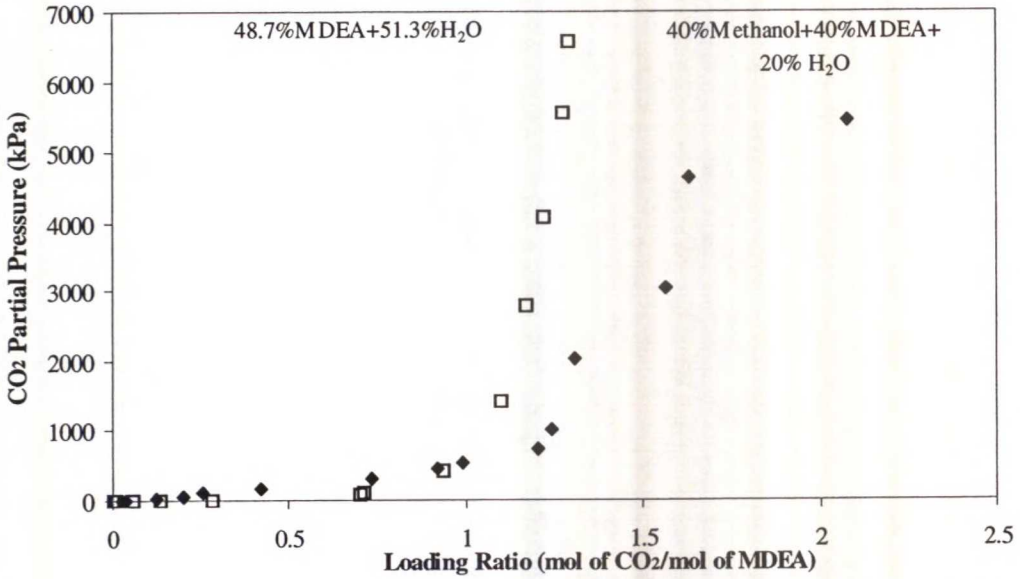

Fig. 4.12 Solubility of carbon dioxide in mixed MDEA solvents at 40 °C: (◆) MDEA (40 wt %) + methanol (40 wt %) + water (20 wt %); (□) MDEA (48.7 wt %) + water (51.3 wt %).[57, 58]

4.3.4 Modelling of solubility of CO_2 in aqueous MDEA solution

A simple model by Posey et al,[59] was tested for predicting of acid gas vapour - liquid equilibrium (VLE) in alkanolamines. The model is valid for total gas loadings (i.e. CO_2 + H_2S) from 0.003 to 0.8, and over a wide range of temperatures and amine concentrations. Being a simple model, it does not use activity coefficients, and it assumes a single combined reaction. The reaction of acid gases with secondary alkanolamines can be expressed approximately by a single equilibrium,

$$RR'NH + CO_2\,(aq) + H_2O \leftrightarrow RR'NH_2^+ + HCO_3^- \qquad (4.32)$$

The H_2S on the other hand reacts rapidly with a following direct proton transfer reaction

$$RR'NH + H_2S(aq) \leftrightarrow RR'NH_2^+ + HS^- \qquad (4.33)$$

The model neglects the presence of carbonate ions since their concentration is very small. The equilibrium constant for reaction (4.32) can be written as follows,

$$K_{CO_2} = [CO_2\ (aq)][Amine] / [HCO_3^-][AmineH^+] \quad (4.34)$$

The [Amine] and [AmineH$^+$] terms can be approximated on a basis of total gas loading, L_T, as

$$[Amine] = (1- L_T)X^0_{Amine} \quad (4.35)$$

$$[Amine\ H^+] = (L_T)X^0_{Amine} \quad (4.36)$$

where X^0_{Amine} is the initial amine concentration neglecting the presence of the acid gases; and $L_T = \alpha_{CO_2} + \alpha_{H_2S}$, where α_{CO_2} and α_{H_2S} are loading of CO_2 and H_2S, respectively.

Henry's law can be expressed as

$$[CO_2\ (aq)] = p_{CO_2} / Hco_2 \quad (4.37)$$

We assume that the bicarbonate mole fraction [HCO_3^-] accounts for all forms of the absorbed CO_2 and replace its symbol with Xco_2, where Xco_2 = [Amine] α_{CO_2}

We combine this with equation (4.34), (4.35), (4.36) and (4.37), and get

$$p_{CO_2} = Kco_2\ [Amine]\ \alpha_{CO_2}\ [L_T/(1- L_T)] \quad (4.38)$$

The equilibrium constant Kco_2, is given as a function of temperature, acid gas loading and amine concentration as below

$$\ln Kco_2 = A + B / T + C\, L_T\, X^0{}_{Amine} + D(L_T\, X^0{}_{Amine})^{0.5} \qquad (4.39)$$

The four regressed parameters for equilibrium constant of CO_2 reaction with MDEA are:[59]

A = 32.45 ± 0.43; B = -7440 ± 146; C = 33 ± 5; D = -18.5 ± 1.6

Only the presence of CO_2 in the absorption reaction was taken into account. Two groups of parameters were tested to take the regression error into consideration. R1 represents A=32.45; B=-7440; C=33; D=-18.5; and R2 represents A= 32.88; B= -7294; C=38; D= -16.9. Using *R1* and *R2* group of parameters, the values of measured[48] partial pressure of CO_2 divided by calculated partial pressure of CO_2 were plotted as a function of the loading ratio of CO_2 at 25°C, 40 °C and 70 °C. (See Figure 4.13).

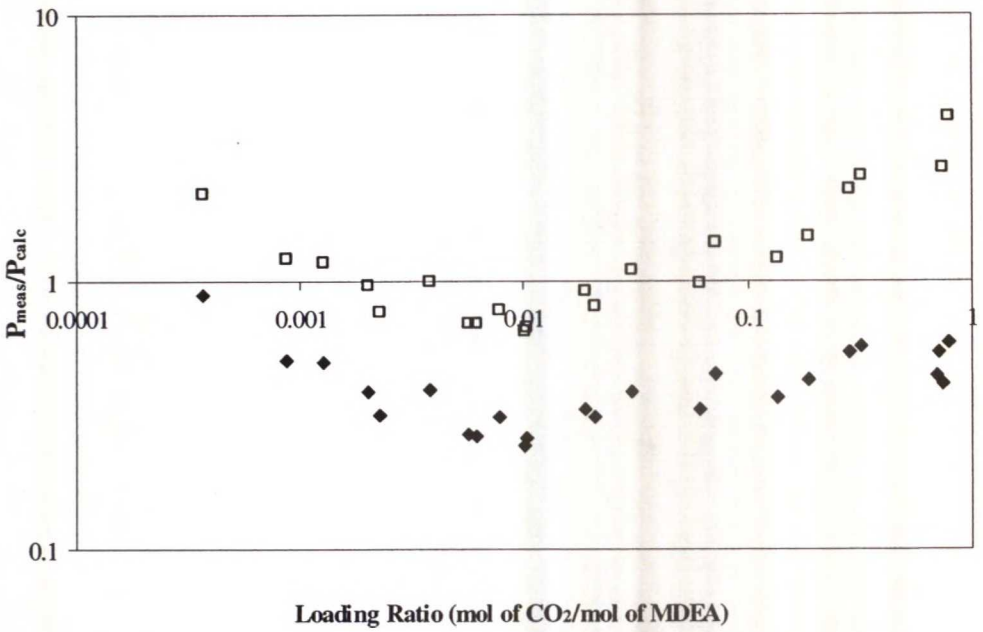

Fig. 4.13 Comparative fit of experimental vapor-liquid equilibrium data to model calculated values for the MDEA – CO_2 system by *R1* and *R2* parameters: (♦) *R1* parameter; (□) *R2* parameter.

We utilize *R1* and *R2* group of parameters with the same datas set, the values of measured partial pressure of CO_2 divided by calculated partial pressure of CO_2 were plotted as a function of the loading ratio of CO_2 at 100 °C and 120 °C is given in Figure 4.14.

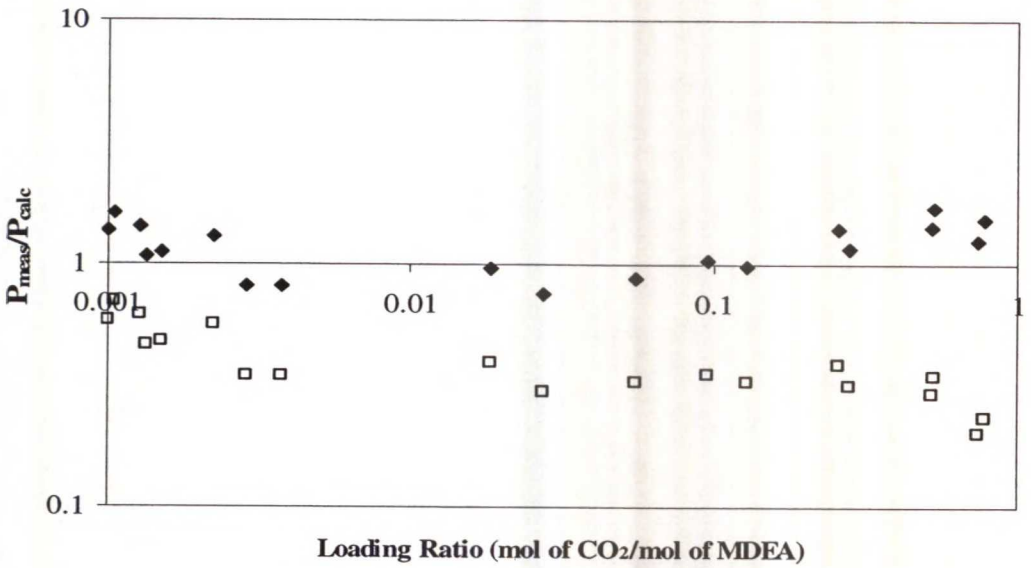

Fig. 4.14 Comparative fit of experimental vapour-liquid equilibrium data to model calculated values for the MDEA – CO_2 system by *R1* and *R2* parameters: (◆) *R1* parameter; (□) *R2* parameter.

Compared predicted values from the model to measured partial pressure of CO_2 in the MDEA system, the data from *R2* set for low temperatures, e.g. 25 °C, 40 °C and 70 °C; and the data from *R1* set for high temperatures like 100 °C and 120 °C, were fitting closely over the entire range of loadings and temperatures. This work is also in good agreement with the work done by Posey et al. [59]

Since natural gas streams and refinery process streams often contain both hydrogen sulphide and carbon dioxide, models for predicting behaviour of the simultaneous absorption H_2S and CO_2 in alkanolamine solutions are essential. The variation in the model use is that total loading is the sum of loading of CO_2 and H_2S. Compared calculated value to measured partial pressure of CO_2 in the presence of H_2S at 40 °C

and 100 °C from Jou et al.[60] can be seen in Figure 4.15. In general, the predicted data by utilizing *R2* parameter are similar to the measured data over the range of loadings.

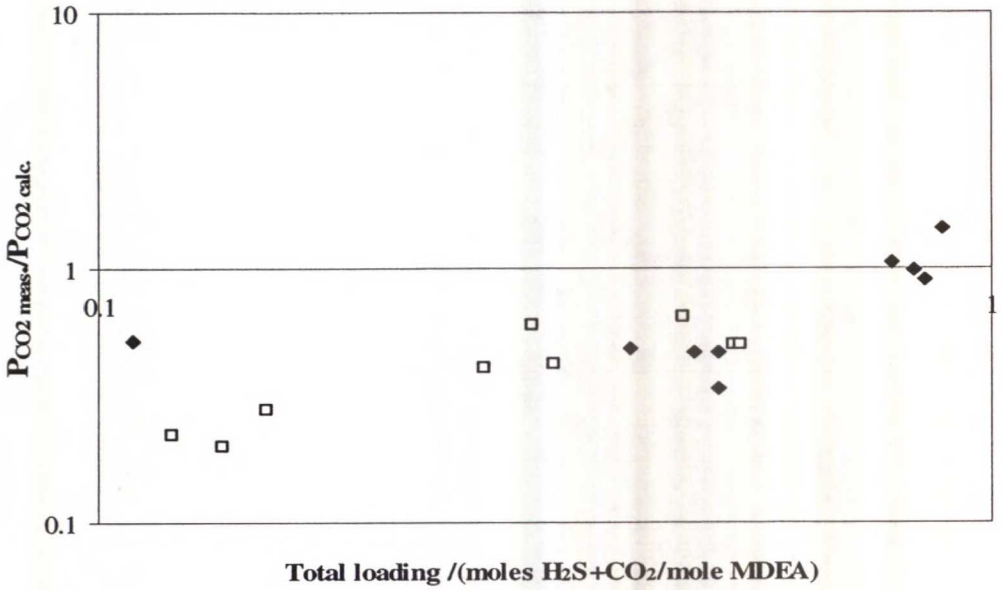

Fig. 4.15 Comparative fit of experimental vapour-liquid equilibrium data to model calculated values for the MDEA – CO_2 system by *R2* parameters.(◆) 40 °C; (□) 100 °C.

4.3.5 The solubility of CO_2 in aqueous AMP solution

A sterically hindered amine is defined structurally as a primary amine where the amino group is attached to a tertiary carbon atom, or a secondary amine in which the amino group is attached to a secondary or tertiary carbon atom. 2-amino-2-methyl-1-propanol (AMP) is one of the typical sterically hindered amines and it is the hindered form of MEA. It has been recently proposed as commercially attractive solvents for the removal of acid gases from gaseous streams. AMP has higher CO_2 removal capacity than MEA at high pressure.[62] Compared to MDEA; AMP has the same CO_2 absorption capacity but has a higher reaction rate constant for the reaction with CO_2.[38, 61]

When AMP reacts with CO_2, an unstable carbamate forms and this carbamate is readily hydrolyzed. As a result, the reaction is mainly the formation of bicarbamate ion.[62, 63] The CO_2 absorption reactions in AMP were described as[61]:

$$CO_2 + RNH_2 \leftrightarrow RNH_2^+COO^- \quad (4.40)$$

$$RNH_2^+COO^- + RNH_2 \leftrightarrow RNHCOO^- + RNH_3^+ \quad (4.41)$$

where R denotes $HO\text{-}CH_2\text{-}C(CH_3)_2$ group.

The solubility of CO_2 in 2M AMP solution is shown in Figure 4.16.[64] At constant temperature the CO_2 partial pressure increases with the CO_2 absorption capacity. Below the value of 0.8 of CO_2 loading ratio, there is little effect of temperature on the solubility. Above 0.8, at a constant CO_2 partial pressure the higher temperature results lower CO_2 absorption capacity.

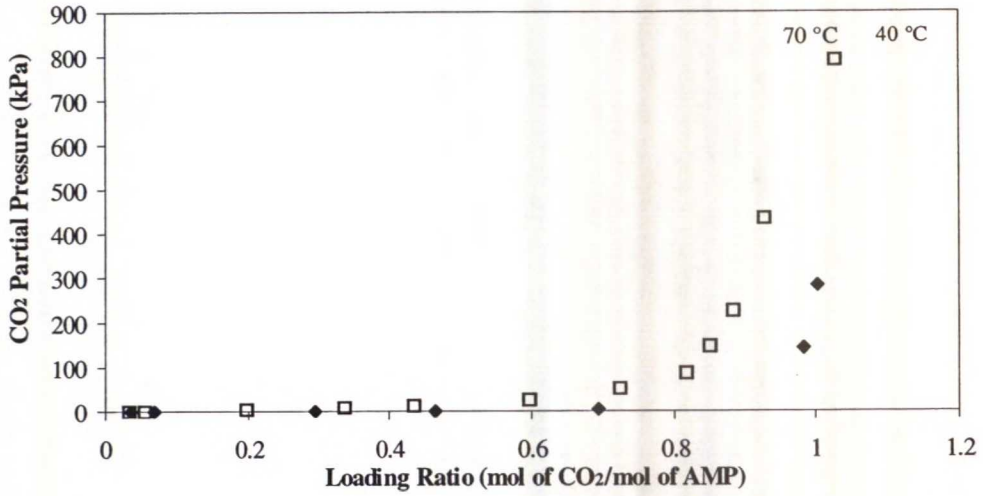

Fig. 4.16 Solubility of carbon dioxide in 2M AMP aqueous solution at different temperatures: (◆) 40 °C; (□) 70 °C.[64]

The solubility of CO_2 in various aqueous AMP solutions at a constant temperature and pressure is shown in Figure 4.17.[65] When the loading is greater than 2 mol of CO_2 /mol of AMP, the solubilities of CO_2 in AMP increase in both solutions; at a

constant partial pressure, CO_2 dissolves much greater in 2.452 M AMP solution than that of 6.477 M.

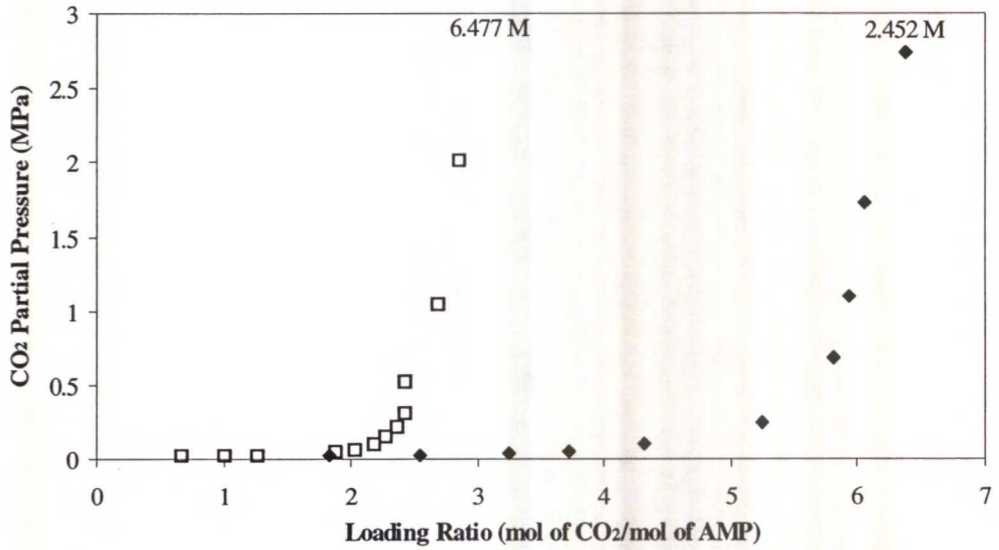

Fig. 4.17 Equilibrium solubility of carbon dioxide in 2.452 M and 6.477 M aqueous AMP solutions at 333.15 K. (◆) 2.451 M; (□) 6.477 M.[65]

4.3.6 The solubility of CO_2 in aqueous mixtures of DEA with AMP

Mixtures of primary or secondary alkanolamine with a tertiary alkanolamine have been used to improve the energy efficiency of the process.[64] Actually, aqueous mixtures of alkanolamines formulated in base of MDEA or sterically hindered alkanolamines are extensively used to remove acid gases.[67]

The selection of the best aqueous mixture of alkanolamines used in acid gases treatment depends a lot on the reaction mechanism. Primary and secondary alkanolamines exhibit high rates of acid-gas removal, and tertiary alkanolamines undergo the much slower acid-base removal because they cannot form the carbamate. With a hindered alkanolamine, e.g. AMP, the carbamate can be formed, but it is unstable. Thus, the principle to use an aqueous mixture of alkanolamines is to maximize high absorption rates, to offer low regeneration costs, and to decrease both corrosion and circulation rates.[68]

The solubilities of CO_2 in the mixture changes regularly. At a given temperature the solubility increases with an increase in pressure. At a given CO_2 partial pressure, it decreases as the temperature increases. See Figure 4.18.[68]

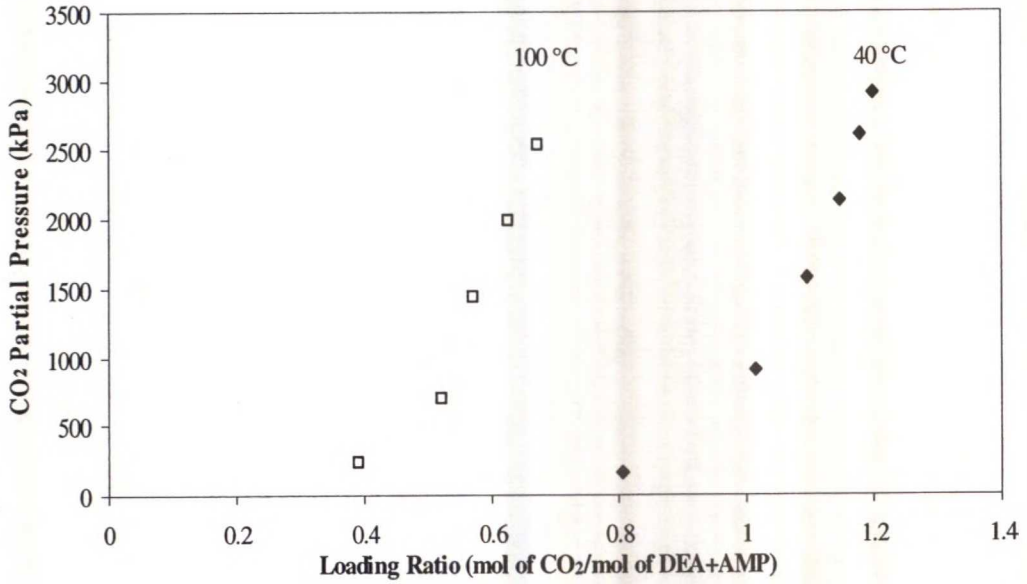

Fig. 4.18 Equilibrium solubility of carbon dioxide in aqueous mixture 25 wt % DEA - 5 wt % AMP at: (♦) 40 °C; (□) 100 °C.[68]

The effect of the amine composition on the solubility of CO_2 is shown from Figure 4.19.[68] At a given pressure, e.g. 250 kPa, the value of loading is 0.862 for the mixture with 5 wt % AMP, and 0.912 for the mixture with 10 wt % AMP. Therefore, we can conclude that the absorption capacity of the blended aqueous amines solution increases as the concentration of the AMP increases, that is, using more hindered alkanolamines are recommended.

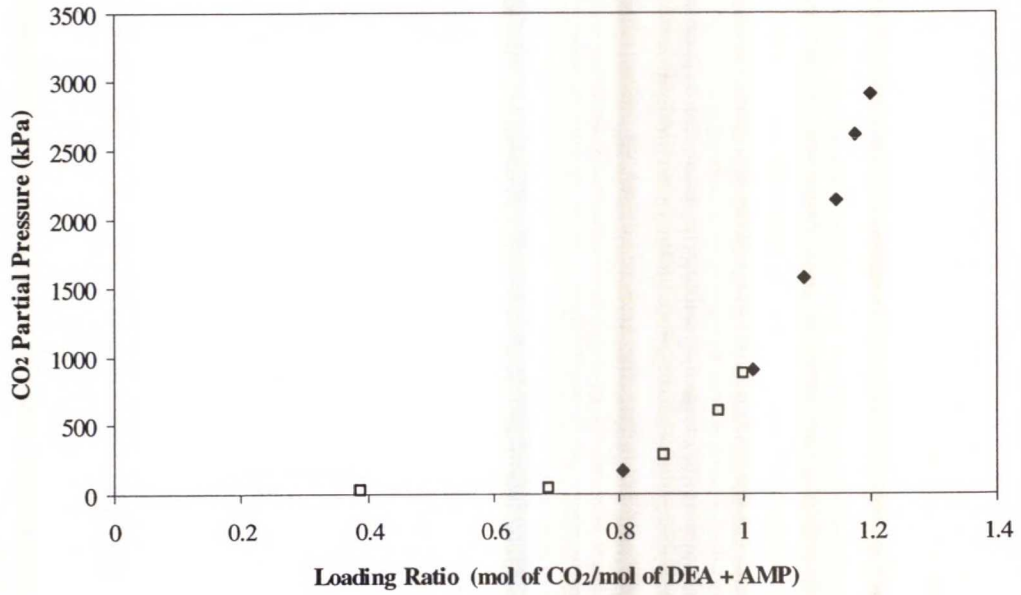

Fig. 4.19 Equilibrium solubility of carbon dioxide in alkanolamine aqueous solutions at 333.15 K: (◆) 25 wt % DEA – 5 wt % AMP; (□) 20 wt % DEA - 10 wt % AMP. [68]

4.3.7 The solubility of CO_2 in aqueous mixtures of MEA with MDEA

Blended amines such as MEA and MDEA contain a combination of the absorption characteristics. MEA achieves stable carbamates and faster reaction rate, but low loading capacity (less than 0.5 mol of CO_2 / mol of amine), on the contrary, MDEA undergoes higher loading capacity and improves energy savings.[44]

A plot of CO_2 partial pressures as functions of the CO_2 loading at a given concentration of mixture of amines by changing temperatures is shown in Figure 4.20.[44] The higher the CO_2 partial pressure, the higher the CO_2 absorption capacity is obtained. The solubility of CO_2 doesn't vary much with the temperatures when the CO_2 loading is smaller than 0.4 mol of CO_2 / mol of mixed amines, but it changes systematically with the temperature at higher loadings. The higher the temperature, the lower the CO_2 solubility.

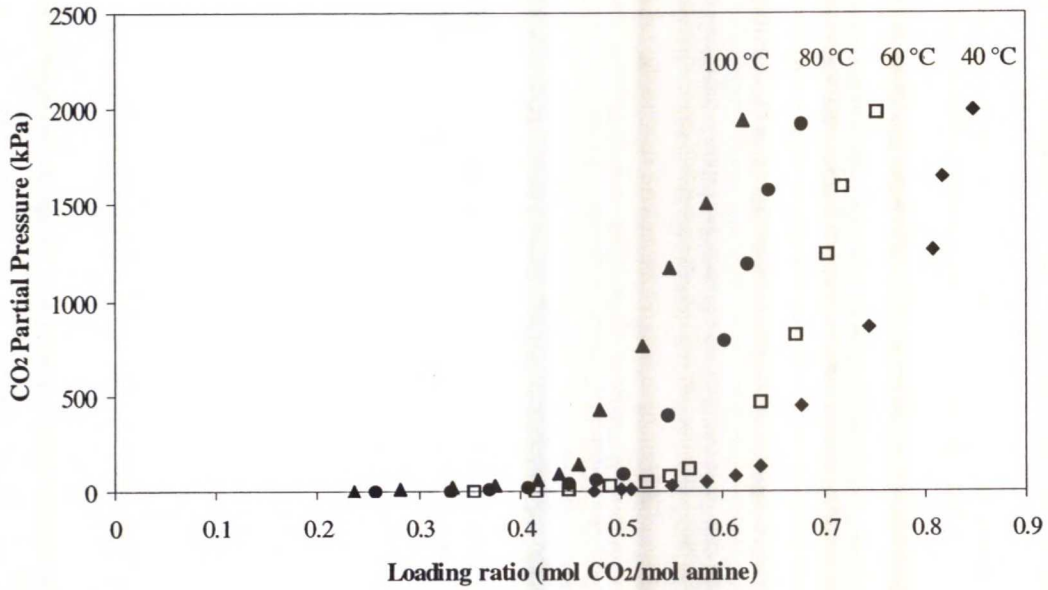

Fig. 4.20 Solubility of carbon dioxide in mixture of 24 wt % MEA + 6 wt % MDEA aqueous solution at: (◆) 40 °C; (□) 60 °C; (•) 80 °C; (▲) 100 °C. [44]

The effects of amine concentrations on CO_2 solubility is included in Figure 4.21.[44] The mixtures considered in the plot are 30 wt % MDEA, 12 wt % MEA + 18 wt % MDEA, 24 wt % MEA + 6 wt % MDEA and 30 wt % MEA. At a given CO_2 partial pressure the solution containing only MDEA shows the greatest CO_2 absorption capacity when the loading is higher than 0.6 mol of CO_2 / mol of mixed amine, and CO_2 absorption capacity in combined MEA and MDEA solution are also greater than that of only comprised of MEA.

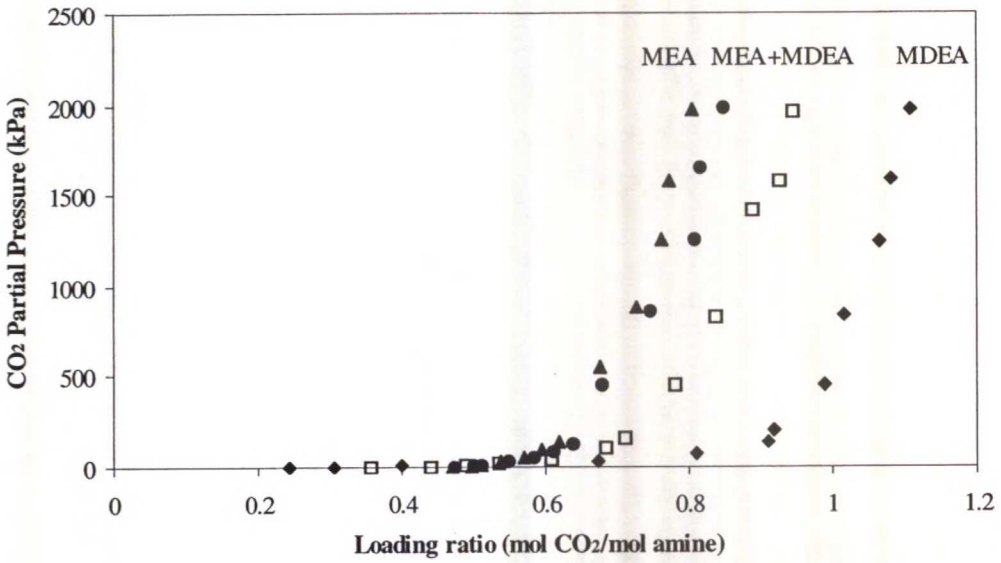

Fig. 4.21 Solubility of carbon dioxide in mixtures of amines aqueous solutions at 40 °C: (♦) 30 wt % MDEA; (□) 12 wt % MEA + 18 wt % MDEA; (•) 24 wt % MEA + 6 wt % MDEA; (▲) 30 wt % MEA. [44]

4.3.8 The solubility of CO_2 in aqueous mixtures of potassium carbonate and physical absorbents

Aqueous alkanolamine and potassium carbonate solutions are typical chemical absorbents used for the removal of acidic gases.[69] CO_2 solubility may increase by that mixing of potassium carbonate and amines. Leites et al [70] studied the CO_2 solubility in aqueous mixtures of K_2CO_3, MEA and H_2O. The effect of adding K_2CO_3 changes the CO_2 solubility more than respective MEA solution.

In particular, aqueous potassium carbonate solutions are commonly used in hot carbonate processes for bulk CO_2 removal because of their large capacity and relative ease of regeneration. In addition, mixed solutions of amines and physical absorbents such as propylene carbonate, can improve gas solubility in high-pressure conditions and save the energy requirements in the regeneration step. Figure 4.22 [69] shows the solubilities of CO_2 in K_2CO_3 solution mixed with propylene carbonate at 50 °C in the CO_2 partial pressure range of 5 kPa to 2 MPa.

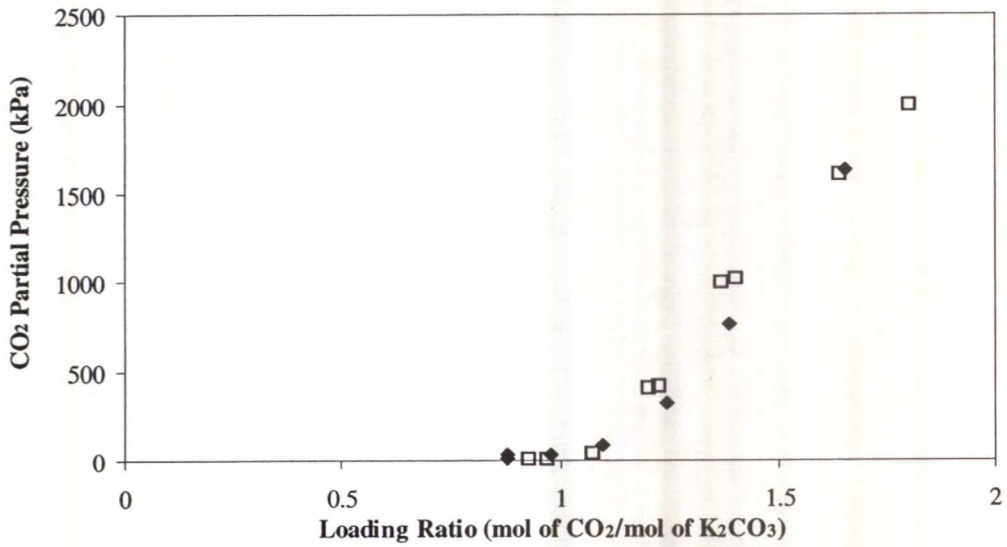

Fig. 4.22 Solubilities of carbon dioxide in aqueous 5 wt % K_2CO_3 - propylene carbonate solutions at 50 °C: (◆) 5 wt % K_2CO_3 - 7.5 wt % propylene carbonate; (□) 5 wt % K_2CO_3 - 15 wt % propylene carbonate.[69]

At constant temperature, the CO_2 solubilities increase as amount of propylene carbonate increase below atmospheric pressure (100 kPa). Above 100 kPa, the CO_2 solubilities decrease with an increase in amount of propylene carbonate.

4.4 Ionic liquids

Room temperature molten salts often referred as ionic liquids (IL) consists typically of an organic cation and inorganic anion. Organic cations are typically quaternary ammonium, phosphonium, pyridinium, and imidazolium salts. Inorganic anions include hexafluorophosphate, tetrafluoroborate, bis(trifluoromethylsulfonyl)imide for example. Ionic liquids have the characteristic of a low melting point; they are thermally stable and have no vapour pressure. That is an advantage in separation processes due to the fact that the ionic liquid solvent is nonvolatile. Development is under away for using ionic liquids as solvents for separation, electrolytes for batteries and fuel cells, phase-transfer reagents, surfactants, and fungicides and biocides, for example.

Some physical properties of ionic liquids, e.g. density, isothermal compressibility, viscosity, heat capacity, and thermal conductivity are important for their potential use in industrial processes. Because ionic liquids are not volatile and will not contaminate the gas stream in even small amounts, this brings the advantage over conventional absorption solvents for separating gases in industry process. Their high thermal stabilities allow the gas separations at higher temperatures than is possible with conventional absorption solvents. In addition, it is possible to use compressed gases or supercritical fluids to separate species from an IL mixture. As an example is recovering a wide variety of solutes from ILs by supercritical CO_2 extraction. The advantage of this is that the solute can be removed quantitatively without any cross-contamination of the CO_2 with an ionic liquid. Such separations should be also possible with other compressed gases, such as C_2H_6, C_2H_4, and SF_6.[71]

Cadena et al.[72] investigated mixtures of CO_2 with 1-n-butyl-3-methylimidazolium hexaflurophosphate ([bmim]-[PF_6]), 1-n-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]), and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf_2N]). The results appear that the ILs with the [Tf_2N] anion had a much greater CO_2 solubility than those with either the [PF_6] or the [BF_4] anion. The effect of ILs anion can be assessed by comparing Henry's constants for these compounds, which can be seen in Figure 4.23. It should be noted that unlike in aqueous solutions the dissolved CO_2 remains in molecular form. Thus no dissociation reactions occur.

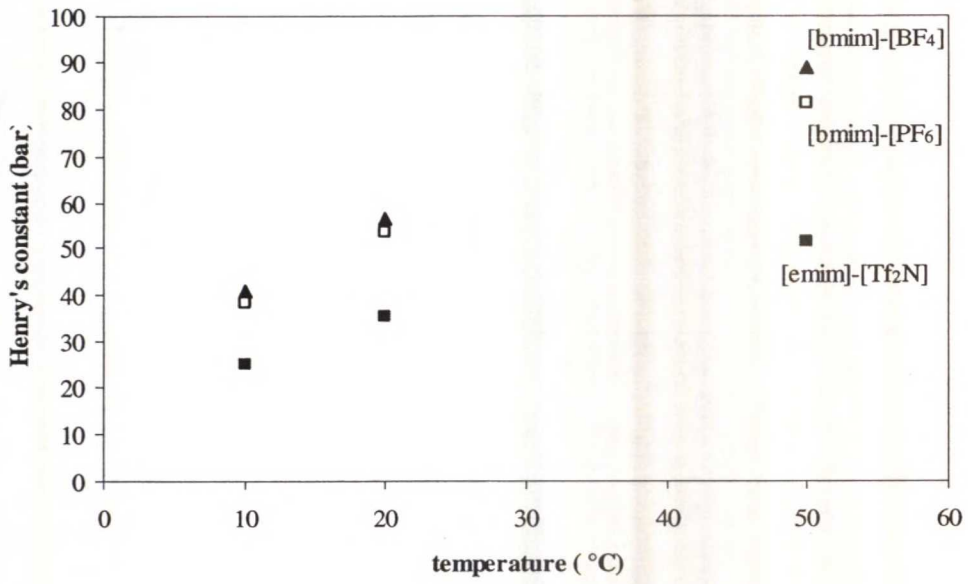

Figure 4.23 Henry's constant for CO_2 solubilities in (■) ([emim][Tf_2N]), (□) [bmim]-[PF_6], (▲) [bmim][BF_4]. [72]

Because of the presence of two fluoroalkyl groups in [Tf_2N] anion, they increase CO_2 solubility in other fluids. These results are entirely consistent with Kazarian and co-workers studies[65] that CO_2 solubility in [bmim][PF_6] and [bmim][BF_4] is governed by interactions with the anion.

5. METAL CARBONATE SYSTEMS

Carbonate minerals have played an important role in the geochemical evolution of Earth.[74] Metal carbonates, calcium carbonate ($CaCO_3$), magnesium carbonate ($MgCO_3$), zinc carbonate ($ZnCO_3$), lead carbonate ($PbCO_3$), and cadmium carbonate ($CdCO_3$) introduced in this work are all sparingly soluble salts. That means that a saturated solution only contains a small number of ions. When an excess of a sparingly soluble compound is added to a solvent, a system in which the solid is in equilibrium with ions in the saturated solution is obtained. [75]

5.1 Solid-liquid-gas equilibrium for metalcarbonates in aqueous systems with dissolved CO_2

Solubilities in aqueous media of sparingly soluble ionic compounds or homogeneous solid mixtures are essential in chemical processes, i.e. dissolution and precipitation reactions, separating and purifying chemicals. In nature, the interactions of the hydrological cycle with the cycle of rocks, dissolution of minerals in water, as well as their precipitation on the ocean floor and in the sediments of rivers and lakes, can be described in terms of solubility equilibria. [33]

When introducing CO_2 into aqueous metal carbonate systems, these reactions occur [76]

$$MCO_3\,(s) \leftrightarrow M^{2+}\,(aq) + CO_3^{2-}\,(aq) \qquad (5.1)$$

$$HCO_3^-\,(aq) \leftrightarrow H^+\,(aq) + CO_3^{2-}\,(aq) \qquad (5.2)$$

$$H_2O + CO_2\,(aq) \leftrightarrow H^+\,(aq) + HCO_3^-\,(aq) \qquad (5.3)$$

$$CO_2\,(g) \leftrightarrow CO_2\,(aq) \qquad (5.4)$$

The overall reaction can be considered as metal carbonate reacts with aqueous acidic solution,

$$M^{2+}CO_3^{2-}(s) + 2\,H^+(aq) \leftrightarrow M^{2+}(aq) + H_2O + CO_2(g)\uparrow \quad (5.5)$$

The complex compounds $M^{2+}(H_xCO_y)^z$ might also be formed as shown in Figure 5.1

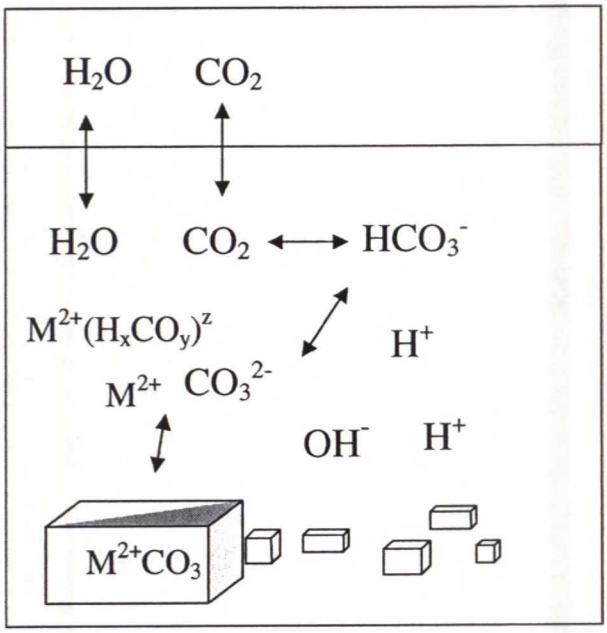

Fig. 5.1 The metal carbonates system in the presence of CO_2 and H_2O.

The solubility equilibrium of a metal carbonate salt $M^{2+}CO_3^{2-}$ in pure water can be expressed as

$$M^{2+}CO_3^{2-}(s) \leftrightarrow M^{2+}(aq) + CO_3^{2-}(aq) \quad (5.6)$$

Solubility product K_{SP} reaction types (5.1) is s as follows: [77]

$$K_{SP} = [M^{2+}]\,[CO_3^{2-}] \quad (5.7)$$

The solubility of a M^{2+} carbonate salt can be increased by introducing protons in the system by adding acids. The M^{2+} carbonate salt can be precipitated by adding electrolytes with anion ligands like: OH^-, HCO_3^-, HS^-, CO_3^{2-}.

For pure and mixed sparingly soluble compounds, solubility products measured in a media of inert or electrolytes at constant ionic strength are advantageous because the activity coefficients of the reacting species are essentially constant. [33]

The relationship between solubility product and equilibrium vapor pressure of the species is obtained as follows,[33]

$$\log K_{ps0}^{I} = \log\{[M^{+2}]\, p_{CO2}\, [H^{+}]^{-2}\} \quad (5.8)$$

where K_{ps0}^{I} is the solubility product at a certain ionic strength.

5.2 *Solubility of carbon dioxide in metal carbonate systems*

5.2.1 CO_2 solubility in calcium carbonate

Amounts of sedimentary deposits of calcium carbonate represent the fossilized remains of earlier marine life, which occur over large parts of the earth's surface. Two types of calcium carbonate deposits exist in the nature, calcite and aragonite. Limestone rock is the most common form of calcite. It is widely used as building material and road aggregate.[78] Precipitated calcium carbonate, calcite is used as a filler in office paper in a paper manufacturing process.[79]

For the system $CaCO_3$-CO_2-H_2O, the following reactions are taken into account for stable phase equilibria: [80]

$$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-} \quad (5.9)$$

$$CO_2\,(g) + H_2O \leftrightarrow H^{+} + HCO_3^{-} \quad (5.10)$$

$$HCO_3^{-} \leftrightarrow H^{+} + CO_3^{2-} \quad (5.11)$$

$$CO_2\,(g) \leftrightarrow CO_2\,(aq) \quad (5.4)$$

The overall reaction is:[81]

$$CaCO_3\,(s) + 2\,H^+ \leftrightarrow Ca^{2+} + H_2O + CO_2\,(g)\uparrow \qquad (5.12)$$

Greenwald suggested [82] that association reactions in $CaCO_3$-CO_2-H_2O system are:

$$Ca^{2+} + HCO_3^- \leftrightarrow CaHCO_3^+ \qquad (5.13)$$

and

$$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-} \qquad (5.14)$$

The association constants of two reactions above are $K_{CaHCO3}{}^+$and K_{CaCO3}, respectively. The temperature dependence of $\log K_{CaHCO3}{}^+$ between 15.1 and 90 °C is given from Plummer et al. [83] as equation (5.15),

$$\log K_{CaHCO3}{}^+ = 1209.12 + 0.31294(T/\mathrm{K}) - 34765.05(\mathrm{K}/T) - 478.782\log(T/\mathrm{K}) \qquad (5.15)$$

where T is in K. $\log K_{CaHCO3}{}^+$ is plotted as a function of temperature in Figure 5.2, the association constant of $CaHCO_3{}^+$ increases with the temperature.

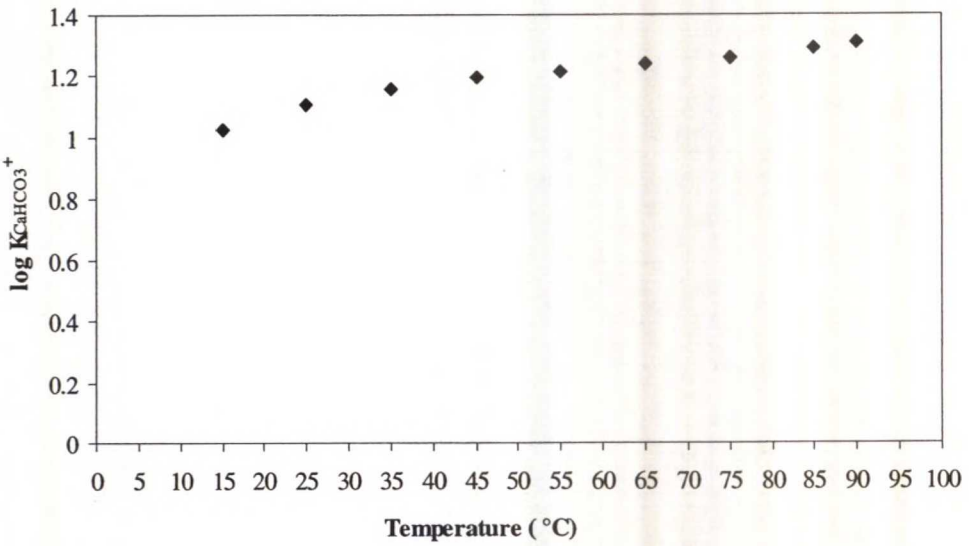

Fig. 5.2 The association constant K_{CaHCO3}^{+} in logarithm forms as a function of temperature.[83]

For reaction $CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$, the log of solubility product of calcite and aragonite between 0 and 90 °C is are given in equations[83] (5.16) and (5.17), respectively.

$$\log K_{CaCO3}^{C} = -171.9065 - 0.077993(T/K) + 2839.319(K/T) + 71.595 \log(T/K) \quad (5.16)$$

$$\log K_{CaCO3}^{A} = -171.9773 - 0.077993(T/K) + 2903.293(K/T) + 71.595 \log(T/K) \quad (5.17)$$

where K_{CaCO3}^{C} and K_{CaCO3}^{A} are solubility products of calcite and aragonite, accordingly.

The plot of temperature dependence of $\log K_{CaCO3}^{C}$ and $\log K_{CaCO3}^{A}$ between 0 and 90 °C is seen in Figure 5.3.

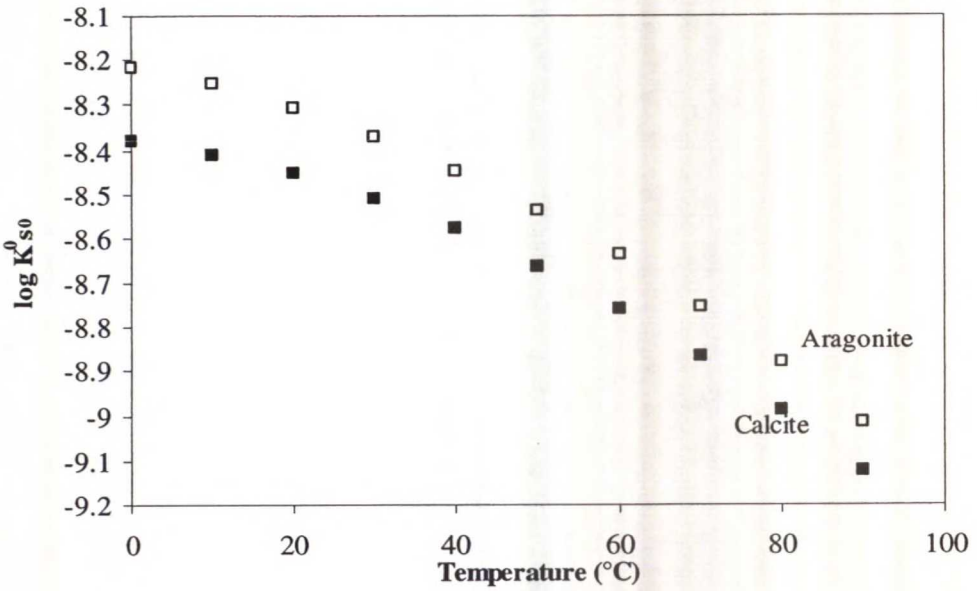

Fig. 5.3 The solubility product constant of $CaCO_3$ as a function of temperature: (■) Calcite; (□) Aragonite. [83]

The solubility constants of both calcite and aragonite decrease with the temperature; however, the values are quite close to each other.

5.2.2 CO_2 solubility in magnesium carbonate

Magnesium carbonate is a light, white, and amorphous powder. It is used in combination with other hydroxides and carbonate compounds. It is practically insoluble in water and alcohol and readily soluble in dilute acid. It is stable in air but slowly absorbs carbon dioxide on exposure in air.[84] Natural magnesium carbonate mineral is industrially important. It is mainly converted by calcinations above 550 °C into different magnesia qualities. Synthetic, magnesium carbonate is utilized in thermal insulating materials, filler in office paper, and additive in the paint and printing ink industry.[79]

For the system $MgCO_3$-CO_2-H_2O, the reactions will occur as following: [76, 85]

$$MgCO_3\,(s) \leftrightarrow Mg^{2+}\,(aq) + CO_3^{2-}\,(aq) \qquad (5.18)$$

$$HCO_3^-(aq) \leftrightarrow H^+(aq) + CO_3^{2-}(aq) \quad (5.19)$$

$$H_2O + CO_2(aq) \leftrightarrow H^+(aq) + HCO_3^-(aq) \quad (5.20)$$

$$CO_2(g) \leftrightarrow CO_2(aq) \quad (5.4)$$

The overall reaction is:

$$MgCO_3(s) + 2H^+(aq) \leftrightarrow M^{2+}(aq) + H_2O + CO_2(g) \uparrow \quad (5.21)$$

When adding $MgCl_2$ into distilled water, it dissolves as:

$$MgCl_2(s) \leftrightarrow Mg^{2+}(aq) + 2Cl^-(aq) \quad (5.22)$$

If CO_2 is introduced into this system, it forms solid $MgCO_3$ and some $Mg(HCO_3)_2$.[85]

$$MgCO_3(s) \leftrightarrow Mg^{2+}(aq) + CO_3^{2-}(aq) \quad (5.18)$$

$$Mg^{2+}(aq) + 2HCO_3^-(aq) \leftrightarrow Mg(HCO_3)_2(aq) \quad (5.23)$$

The solubility product of $MgCO_3$ is given as $1 \cdot 10^{-5}$ $(mol/kg)^2$ at 25°C.[86]

Kang et al.[87] gives the phase equilibria for H_2O-$MgCl_2$-CO_2 system at the $MgCl_2$ concentration ranges of 3-10 mass % and at the temperature and pressure ranges of 272-282 K and 15-45 bars, respectively. (See Figure 5.4) Hydrate dissociation pressure is increasing with the temperature; at a constant temperature, the higher the concentration range of electrolytes $MgCl_2$, the higher hydrate dissociation pressure is obtained.

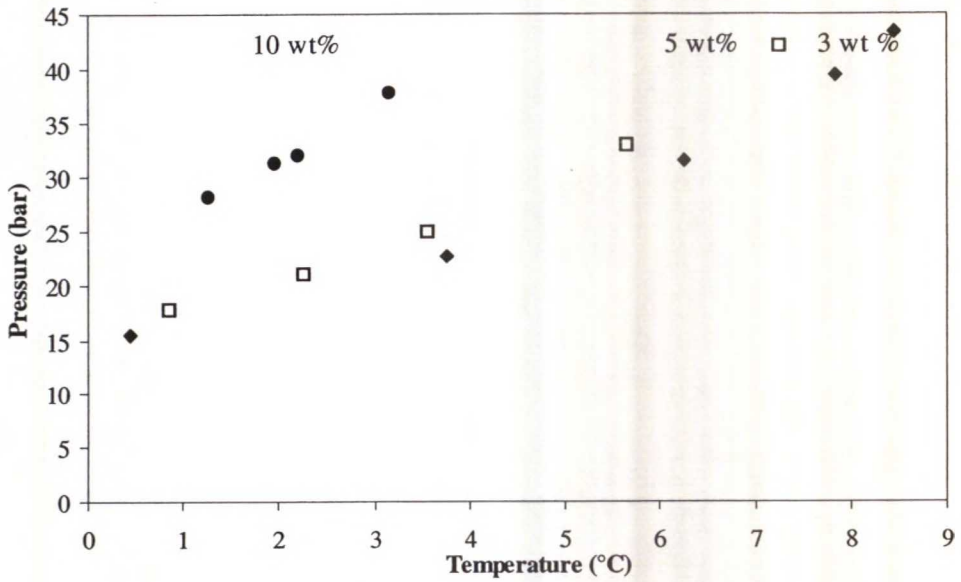

Fig. 5.4 Equilibrium hydrate dissociation pressure of H_2O-$MgCl_2$-CO_2 system: (◆) 3 wt % $MgCl_2$; (□) 5 wt % $MgCl_2$; (●) 10 mass % $MgCl_2$.[87]

5.2.3 CO_2 solubility in zinc carbonate

Zinc carbonate is colourless hexagonal crystal. The most common zinc carbonate in the nature is Smithsonite.[88] It is an important sparingly soluble transition metal carbonate for both geochemical and industrial process. [89] In dilute strong acid media, reactions occur as following:[88]

$$ZnCO_3\,(s) \leftrightarrow Zn^{2+}\,(aq) + CO_3^{2-}\,(aq) \qquad (5.24)$$

$$HCO_3^-\,(aq) \leftrightarrow H^+\,(aq) + CO_3^{2-}\,(aq) \qquad (5.25)$$

$$H_2O + CO_2\,(aq) \leftrightarrow H^+\,(aq) + HCO_3^-\,(aq) \qquad (5.26)$$

$$CO_2\,(g) \leftrightarrow CO_2\,(aq) \qquad (5.4)$$

The overall reaction is

$$ZnCO_3\,(s) + 2\,H^+\,(aq) \leftrightarrow Zn^{2+}\,(aq) + H_2O + CO_2\,(g)\uparrow \qquad (5.27)$$

According to equation (5.8), the solubility of zinc carbonate depends on temperature, ionic strength, pH, and partial pressure of carbon dioxide.

Egorov and Titova[88] studied the solubility product constants for $ZnCO_3$ in aqueous CO_2 solution in the temperature range 298 K to 373 K as equation (5.28).

$$\log K_{so}^{0} = -31.77 + 1480 / (T / K) + 7.17 \log (T / K) - (2.82 \cdot 10^{-3})\,(T / K) \qquad (5.28)$$

$\log K_{so}^{0}$ plotted as a function of temperature is shown in Figure 5.5. The solubility product of $ZnCO_3$ slightly decreases with the temperature.

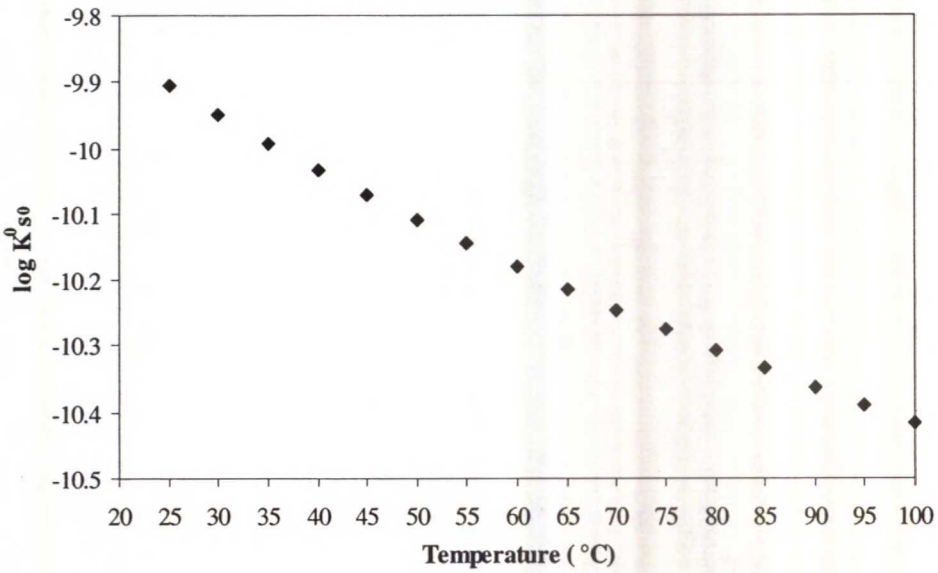

Fig. 5.5 The solubility product constant of $ZnCO_3$ as a function of temperature. [88]

Smith's[90] reported values of partial pressure of CO_2 as a function of solubility of $ZnCO_3$ at 298.15 K. His values are shown in Figure 5.6. Under the condition that ionic strength is zero, solubility of $ZnCO_3$ increases as carbon dioxide partial pressure increases, and the major solution species at high carbon dioxide partial pressure is HCO_3^-.

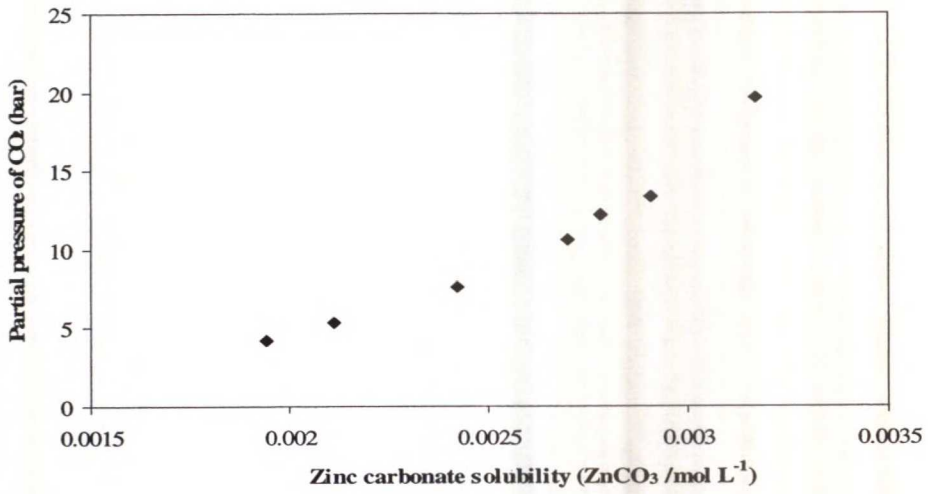

Fig. 5.6 The solubility of zinc carbonate in aqueous solution containing carbon dioxide at 298.15 K. [90]

5.2.4 CO_2 solubility in lead carbonate

Lead carbonate exists as cerussite in the nature. The mineral cerussite has an orthorhombic crystal structure.

$$PbCO_3\,(s) \leftrightarrow Pb^{2+}\,(aq) + CO_3^{2-}\,(aq) \qquad (5.29)$$

$$HCO_3^-\,(aq) \leftrightarrow H^+\,(aq) + CO_3^{2-}\,(aq) \qquad (5.30)$$

$$H_2O + CO_2\,(aq) \leftrightarrow H^+\,(aq) + HCO_3^-\,(aq) \qquad (5.31)$$

$$CO_2\,(g) \leftrightarrow CO_2\,(aq) \qquad (5.4)$$

In acidic solution, the overall reaction occurs:[91]

$$PbCO_3\,(s) + 2\,H^+\,(aq) \leftrightarrow Pb^{2+}\,(aq) + H_2O + CO_2\,(g)\uparrow \qquad (5.32)$$

Egorov and Titova [91] derived the equation for solubility product of $PbCO_3$ for the reaction (5.29), in the range 273 K to 373 K:

$$\log K_{so}^{0} = -24.04 - 805 / (T / \mathrm{K}) + 5.86 \log (T / \mathrm{K}) - 2.41 \cdot 10^{-3} (T / \mathrm{K}) \qquad (5.33)$$

$\log K_{so}^{0}$ plotted as a function of temperature is shown in Figure 5.7. The solubility product of $PbCO_3$ slightly increases with the temperature.

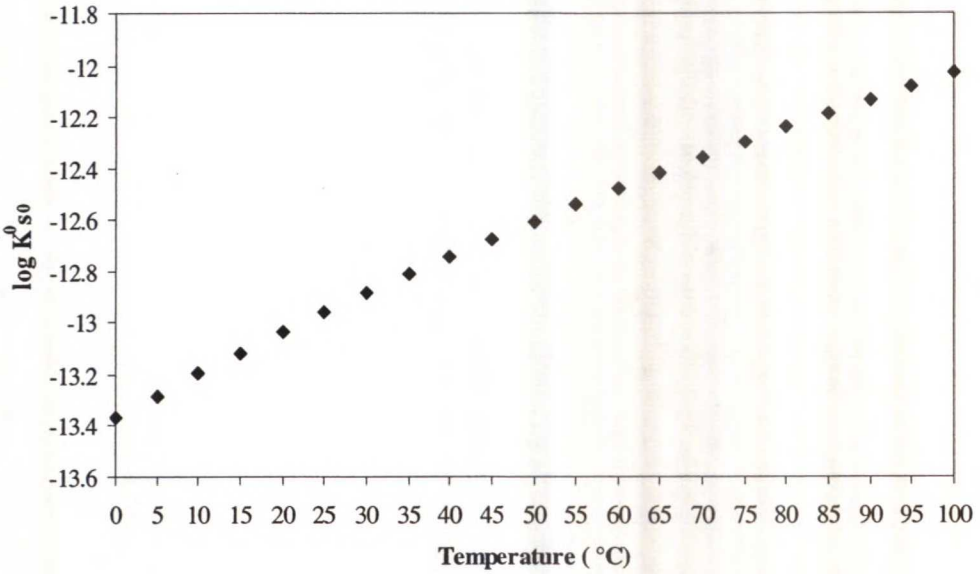

Fig. 5.7 The solubility product of $PbCO_3$ as a function of temperature.[91]

Pleissner[91] measured the effect of the presence of dissolved carbon dioxide on the solubility of lead carbonate at 291.15 K. His results are shown in Figure 5.8.[91] As can be seen, pressure of carbon dioxide increases with the concentration of $PbCO_3$.

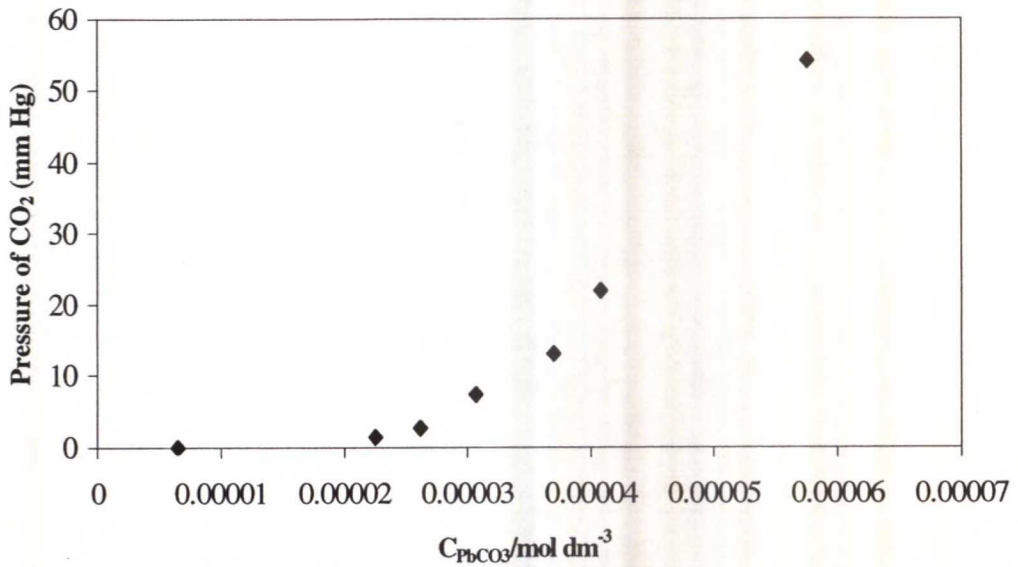

Fig. 5.8 The solubility of lead carbonate in aqueous solution containing carbon dioxide at 291.15 K.[91]

5.2.5 CO_2 solubility in cadmium carbonate

Cadmium carbonate is a colourless hexagonal crystal, the naturally occurring cadmium carbonate mineral is otavite.[88] Commercially available cadmium carbonate contains various trace inorganic contaminants, which has effect on dissolution. Thus synthesised $CdCO_3$ is recommended.[84] The reactions occurring for the system $CdCO_3$-CO_2-H_2O are:[88]

$$CdCO_3\,(s) \leftrightarrow Cd^{2+}\,(aq) + CO_3^{2-}\,(aq) \qquad (5.34)$$

$$HCO_3^-\,(aq) \leftrightarrow H^+\,(aq) + CO_3^{2-}\,(aq) \qquad (5.35)$$

$$H_2O + CO_2\,(aq) \leftrightarrow H^+\,(aq) + HCO_3^-\,(aq) \qquad (5.36)$$

$$CO_2\,(g) \leftrightarrow CO_2\,(aq) \qquad (5.4)$$

In acidic solutions, reactions occurs

$$CdCO_3\,(s) + 2\,H^+\,(aq) \leftrightarrow Cd^{2+}\,(aq) + H_2O + CO_2\,(g)\uparrow \qquad (5.37)$$

Egorov and Titova[88] studied the solubility product of $CdCO_3$ for the reaction (5.34) at temperature range 273.15 K to 373.15 K as:

$$\log K_{so}^{0} = -28.06 + 619 / (T / \mathrm{K}) + 6.22 \log (T / \mathrm{K}) - (2.35 \cdot 10^{-3}) (T / \mathrm{K}) \qquad (5.38)$$

$\log K_{so}^{0}$ plotted as a function of temperature is shown in Figure 5.9.[88] As can be seen, there is a shallow minimum K_{so}^{0} value at 45 °C, after that, the solubility product of $CdCO_3$ slightly increases with the temperature.

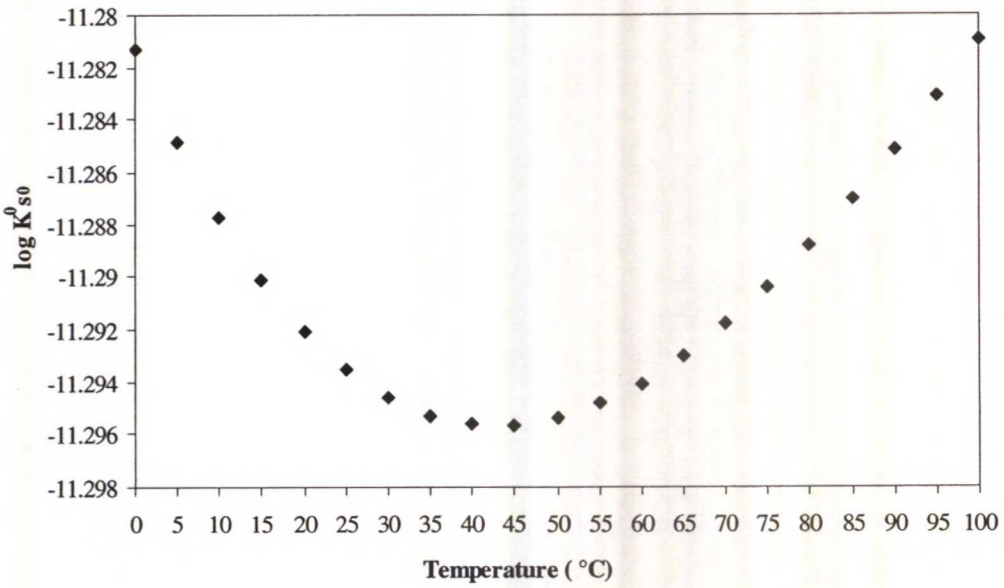

Fig 5.9 The solubility product constant of $CdCO_3$ as a function of temperature.[88]

The solubility of cadmium carbonate in water at 298.15 K was studied by Kelly et al[88] and Jaulmes et al.[88] (See Figure 5.10) The higher the CO_2 partial pressure, the greater the solubility of cadmium carbonates.

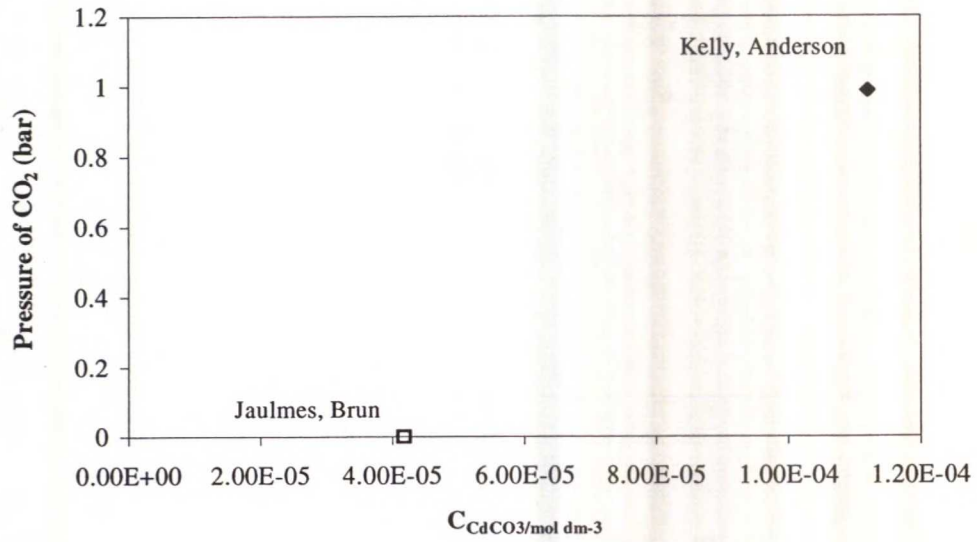

Fig. 5.10 The solubility of cadmium carbonate in water. [88]

At 25 °C the solubility product values of these metal carbonates show that $MgCO_3$ is the most soluble compound, and $PbCO_3$ is least soluble. Combining the studies above as shown in Figure 5.11, we see that, solubility product of $PbCO_3$ is increasing with the temperature; $CaCO_3$ and $ZnCO_3$ are deceasing with that of the temperature; $CdCO_3$ is first decreasing, when the temperature reaches 45 °C, it starts to increase. But overall, it is obvious that $PbCO_3$ is the least soluble compound, and both $MgCO_3$ $CaCO_3$ are much soluble than those of $PbCO_3$, $ZnCO_3$, and $CdCO_3$.

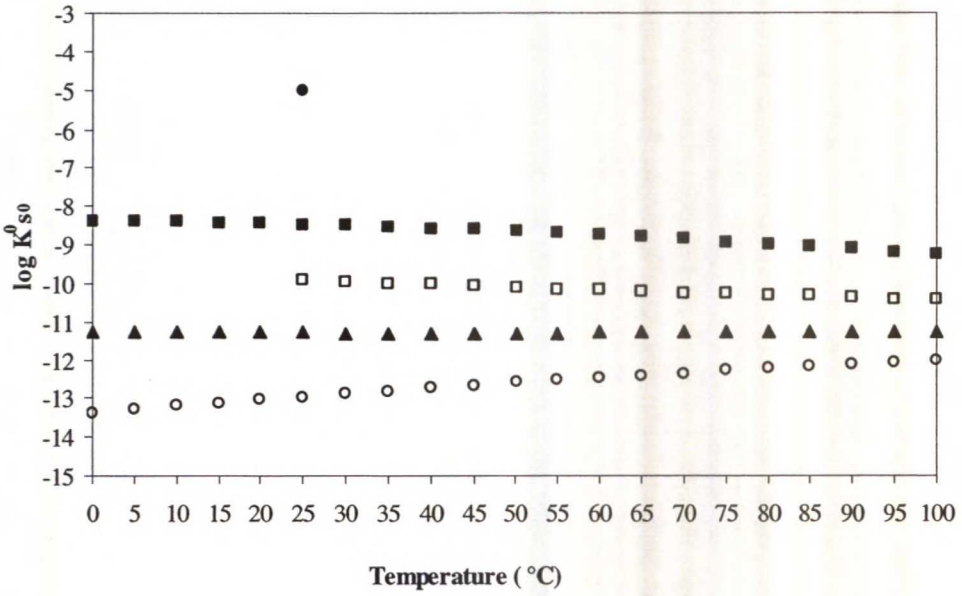

Fig 5.11 The logarithm of solubility product values of the studied metal carbonates as a function of temperature: (●) $MgCO_3$;[86] (■) Calcite;[83] (□) $ZnCO_3$;[88] (▲) $CdCO_3$;[88] (○) $PbCO_3$.[91]

6. SIMULATIONS

6.1. The Debye-Hückel theory of electrolyte solutions

In 1923, Debye and Hückel introduced quantitative representation of the distribution of the ions in an electrolyte solution. They used a model of complete ionisation to rigid spherically symmetrical ions in a continuous medium with the macroscopic permittivity of the solvent. In this model, a central ion was chosen. The interactions between ions and solvent molecules were ignored. [93, 94]

The Debye-Hückel theory applies in very dilute solution which concentration is up to about molalities of 0.01, but its modification can be used in more concentrated aqueous solutions about molalities of 1.[95]

6.2 The Pitzer model

Pitzer and his co-workers presented models for predicting the mean ionic activity coefficients of salts in aqueous electrolytes solutions as a function of the molality.[96] The Pitzer model has been applied successfully to aqueous electrolyte solutions for which those component-dependent interaction parameters have been derived and tabulated.[97] It can be used in non-idealities aqueous solutions, which brings some industrially importance. [98, 99]

6.2.1 The Pitzer equation

Pitzer equation proposed the unsymmetric excess Gibbs free energy of aqueous electrolyte systems. The basic equation is:

$$\frac{G^{ex^*}}{n_w RT} = f(I) + \sum_i \sum_j \lambda_{ij}(\mathrm{I})\, m_i m_j + \sum_i \sum_j \sum_k \mu_{ijk} m_i m_j m_k \qquad (5.24)$$

The function *f(I)* is a modified Debye-Hückel term, and it is a function of ionic strength, temperature and solvent properties. The empirical form by Pitzer for *f(I)* is:

$$f(I) = -\,A_\phi \frac{4I}{1.2} \ln\left(1 + 1.2\sqrt{I}\right) \qquad (5.25)$$

with

$$I = (1/2) \sum_i m_i z_i^2 \tag{5.26}$$

A_ϕ is the osmotic Debye-Hückel parameter. The parameters λ_{ij} are second virial coefficients giving the effects of short-range forces between solutes i and j; the parameters μ_{ij} are corresponding third virial coefficients for the interactions of three solutes i, j, and k. The second virial coefficients are functions of ionic strength. Dependence of the third virial coefficients on ionic strength is neglected. The λ and μ matrices are taken to be symmetric. [99]

6.2.2. The modified Pitzer equation

Pitzer modified the basic equation by defining a new set of parameters representing certain combinations of the second and third virial coefficients. The modified Pitzer equation is given by (5.27)

$$\frac{G^{ex^*}}{n_W RT} = f(I) + \sum_C \sum_{C'} m_C m_{C'} (\theta_{CC'} + \sum m_a \Psi_{CC'a}) + \sum \sum m_a m_{a'} (\theta_{aa'} + \sum_C m_C \Psi_{aa'C})$$
$$+ 2 \sum_C \sum_a m_C m_a \left[B_{Ca}(I) + \sum_C m_C Z_C c_{Ca}) / \sqrt{Z_C Z_a} \right] \tag{5.27}$$

The new parameters B and θ are binary ion-ion parameters and C and ψ are ternary ion-ion parameters. The ion-ion interaction parameters, B and C, are characteristic of each aqueous mixed-electrolyte system. [99]

The modified Pitzer model is more useful for many pure electrolytes and mixed strong aqueous electrolyte systems, which the concentration is up to molalities of 6. [94]

6.3 CO_2 solubility simulations using Chemsheet programme

Chemsheet programme[100] is used in modelling CO_2 solubility in multi-phase equilibrium system (gas-aqueous solution-solids) Na-Ca-Mg-Zn-Pb-Cd-H-Cl^--OH^--HCO_3^--CO_2-O_2- H_2O at 25 °C.

6.3.1 CO_2 solubility in metal chloride system

In this work, Henry's constants for CO_2-H_2O system were modelled at 298.15 K, and the value is 161.5 MPa. According to Equation (4.17), the calculated Henry's constant is 161.97 MPa. The results are very similar.

The solubility of CO_2 in single electrolyte aqueous NaCl, $MgCl_2$, $CaCl_2$ solution are plotted in Figure 6.1.

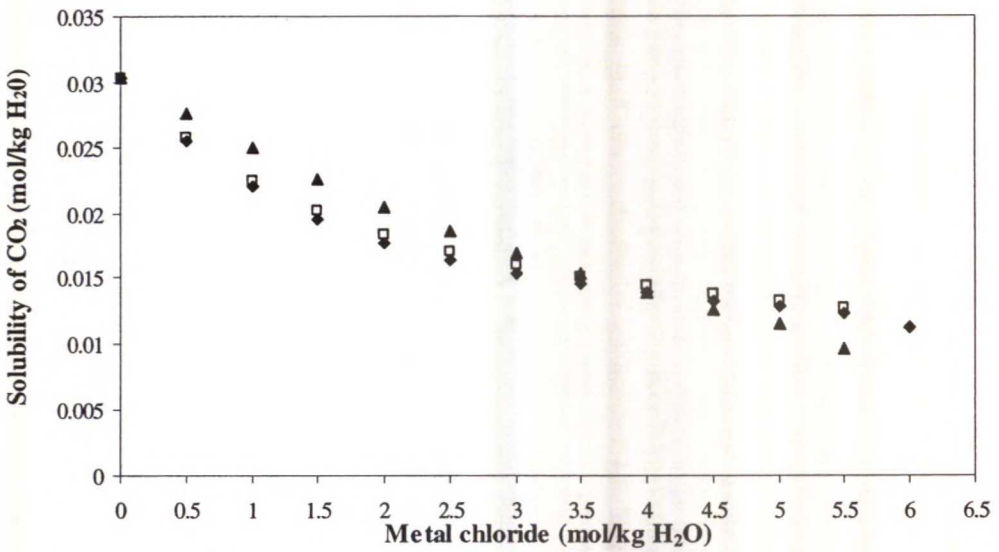

Fig. 6.1 Modelling of CO_2 solubility in aqueous metal chloride solution: (◆) $MgCl_2$; (□) $CaCl_2$; (▲) NaCl.

Comparing to Harvie et al[101] in Figure 6.2, the solubility of CO_2 decreases with increasing concentration of $MgCl_2$, NaCl and $CaCl_2$. The modelled values are in good agreement with literature.

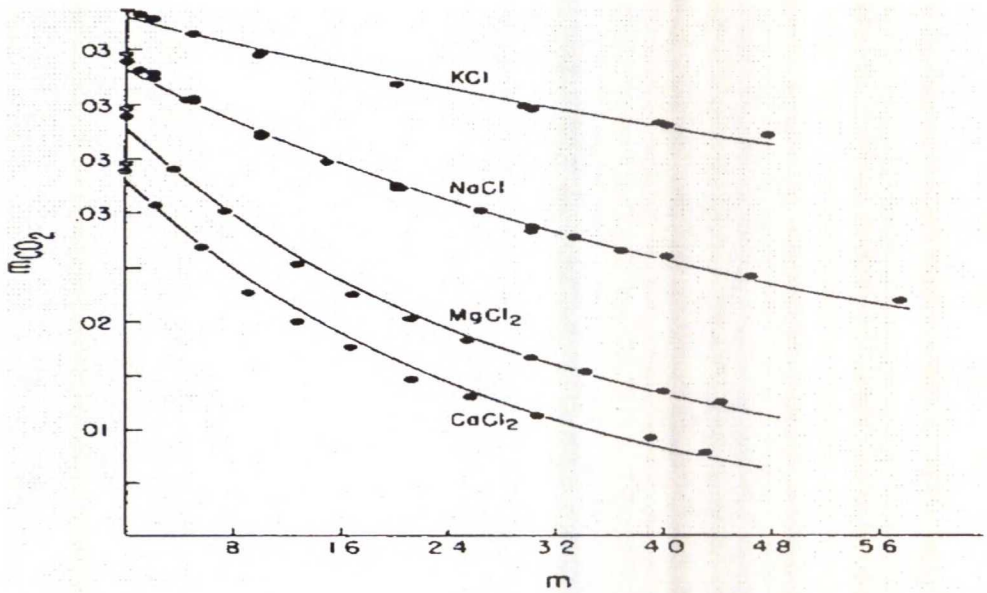

Fig. 6.2 The solubility of carbon dioxide in single electrolyte aqueous solution and molality is in unit mol/kg H_2O. (The numerical values in the y-axis are in the range of 0 to 0.03) [101]

6.3.2 CO_2 solubility in metal carbonate system

For $PbCO_3 - CO_2 - H_2O$ system, partial pressure of CO_2 is calculated as a function of CO_2 concentration. (See Figure 6.3) Modelling 1 by using entropy S = 141 (J / mol K) is quite close to the values from Pleissner[91]; but modelling 2 by S = 131 (J / mol K) which is from Pitzer data file differs a bit from Pleissner[91]. It is concluded that changing thermodynamic data, e.g. entropy, can lead to different results. Since it is hard to know the exact thermodynamic values of $PbCO_3$, we could only assume that different entropy values make the modelling different from the literature.

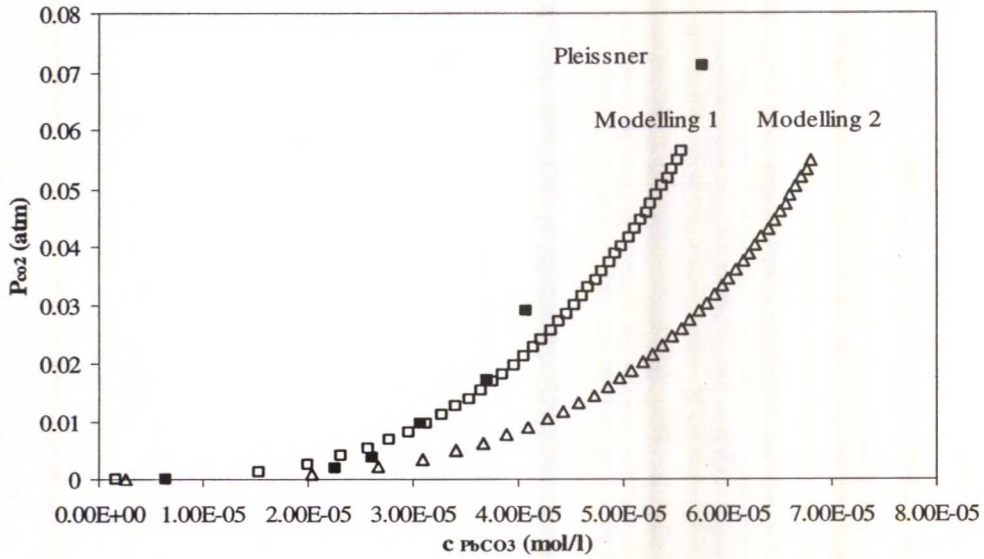

Fig. 6.3 Partial pressure of CO_2 as a function of CO_2 concentration at 291.15 K: (■)Pleissner[91]; (□) Modelling 1 by S = 141 (J / mol K) ; (Δ) Modelling 2 by S = 131 (J / mol K).

For $CdCO_3$ (otavite) – CO_2 – H_2O system, concentration of Cd^{2+} is calculated as a function of pH value. See Figure 6.4.

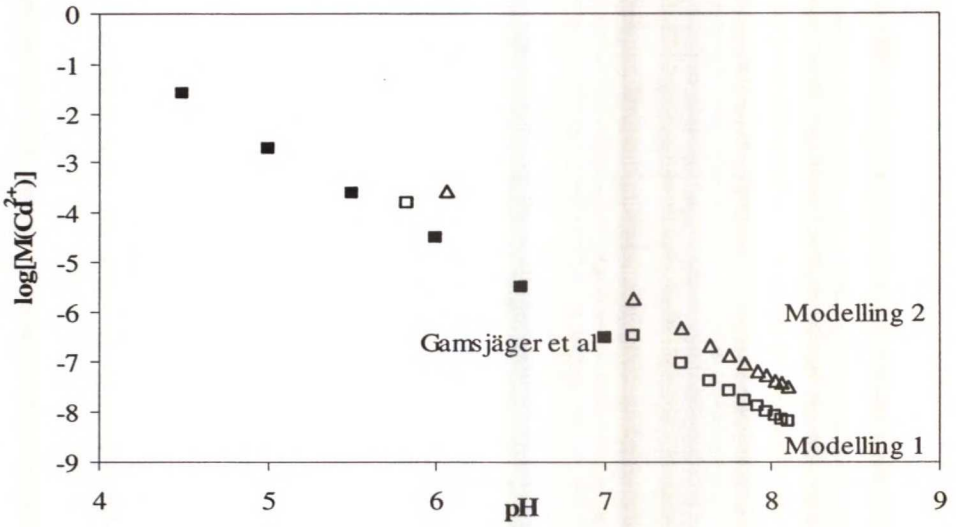

Fig. 6.4 Solubility of $CdCO_3$ at 25 °C: (■) Gamsjäger et al;[76] (□) Modelling 1 by S = 106 (J / mol K) ; (Δ) Modelling 2 by S = 92.466 (J / mol K).

The values of enthalpy and entropy of otavite given by Stipp et al.[102] differ from that of Pitzer database, see table 6.1. As can be seen from figure 6.4, similarly with $PbCO_3$, the values of log[M(Cd^{2+})] of modelling 1 by using entropy S = 106 (J / mol K) from Stipp et al[102] are quite close to the values from Gamsjäger et al[76]; but modelling 2 by S = 92.466 (J / mol K) which is from Pitzer data file are bigger than that of Gamsjäger et al[76].

Table 6.1 The comparison of values for thermodynamic properties for the formation of otavite, $CdCO_{3(s)}$ at T = 298.15 K; P = 1 atm.

Species	$\Delta H°_f$ (kJ/mol)	$S°$ (J / mol K)	Ref.
$CdCO_{3(s)}$	- 751.910	106	Stipp et al[102]
$CdCO_{3(s)}$	- 751.864	92.466	this work
Cd^{2+}	- 75.9	- 72.8	Stipp et al[102]
Cd^{2+}	-75.898	- 72.8	this work
CO_3^{2-}	- 675.23	- 50.0	Stipp et al[102]
CO_3^{2-}	- 675.23	- 49.999	this work

7. CONCLUSIONS AND SUGGESTIONS

For the solubility of CO_2 in the alkanolamine systems, at constant pressure, the solubility of CO_2 per mole amine decreases with increasing temperature; at a constant CO_2 partial pressure, CO_2 solubilities decrease with increasing concentration of amine. Mixtures of primary or secondary alkanolamine with a tertiary alkanolamine or sterically hindered alkanolamines can improve the capacities of absorbing acid gases. Typical chemical absorbents, e.g. mixtures of aqueous alkanolamine and potassium carbonate solutions are used to increase the CO_2 solubility than by using only single amine solution. At high pressures, mixed solutions of amines and physical absorbents such as propylene carbonate, can improve CO_2 solubility when comparing with amine solutions. In addition, ionic liquids may be also optional solvents for separating CO_2 from other gas species in industry; ionic liquids with $[Tf_2N]$ anion bring much greater CO_2 solubility than those with $[PF_6]$ or the $[BF_4]$ anion due to the presence of two fluoroalkyl groups in $[Tf_2N]$ anion.

The results of calculating CO_2 solubility in aqueous metal chloride solutions $MgCl_2$, NaCl, and $CaCl_2$ by using Pitzer model fit rather well with the literature. The values from calculating solubilities of CO_2 in aqueous $PbCO_3$ solution by using Pitzer model are a little bit different due to the difference of thermodynamic values. Similarly, CO_2 in aqueous $CdCO_3$ solution by modelling is also different from the literature, since the thermodynamic data from different sources are not the same.

Measurements of the CO_2 solubility in aqueous metal carbonate systems should be performed in the future, in order to compare with the values of modelling. More accurate thermodynamic data and Pitzer parameters are needed for improving the reliability of the calculations.

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APPENDIX:

Data-file of Pitzer model for equilibrium system Na-Ca-Mg-Zn-Pb-Cd-H-Cl^--OH^--HCO_3^--CO_2-O_2- H_2O at 25 °C.

```
§
 11  2  4  25 23
C                 O                 H
Ca                Cl                Cd
Mg                Na                Pb
Zn                EA
    12.0110            15.9990            1.0080
    40.0800            35.4530          112.4100
    24.3050            22.9900          207.2000
    65.3800             0.0010
 6  1  2  3  4  5  6
 1  2
GASES
IDMX
CO2(g)
 7 2  1.0  2.0  0.0  0.0  0.0  0.0  0.0  0.0  0.0  0.0  0.0
-393505.20     213.76890
 500.00000     22.226160     0.56200480E-01 -.22518390E-04  10489.170
0.00000000
 5000.0000     53.137770     0.48180580E-02 -.53776350E-06 -2917744.0
H(g)
 7 1  0.0  0.0  1.0  0.0  0.0  0.0  0.0  0.0  0.0  0.0  0.0
 217999.00     114.71690
 6000.0000     20.790300     0.00000000     0.00000000     0.00000000
H2O(g)
 7 3  0.0  1.0  2.0  0.0  0.0  0.0  0.0  0.0  0.0  0.0  0.0
-241826.80     188.83230
 600.00000     33.568230     -.42007360E-02 0.14761150E-04 0.00000000
0.00000000
 1600.0000     21.869770     0.22560130E-01 -.39999040E-05  848933.60
0.00000000
 6000.0000     51.191240     0.26903120E-02 -.17991200E-06 -18020070.
O2(g)
 7 2  0.0  2.0  0.0  0.0  0.0  0.0  0.0  0.0  0.0  0.0  0.0
0.00000000     205.14570
 298.15000     29.430990     -.40152550E-02 0.12820260E-04 -407.57410
0.00000000
 5000.0000     31.011860     0.41902980E-02 -.38482870E-06 -285763.80
AQUEOUS
PITZ
H2O
```

7 2 0.0 0.0 1.0 2.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0
-285830.00 69.948110
372.78000 59.688940 0.23012000E-01 0.24760910E-04 587015.20
0.00000000
500.00000 16.748550 0.62119850E-01 0.90391140E-04 3279838.0
CO2(a)
7 1 0.0 1.0 2.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0
-413839.50 117.61220
398.00000 0.00000000 1.2065330 0.00000000 0.00000000
CO3(-2a)
7 2 -2.0 1.0 3.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 2.0
-675234.80 -49.999000
333.15000 69525.340 -287.93830 0.33477810 -.12200130E+10
0.00000000
473.15000 -4130.3740 18.287980 -.23649400E-01 47155020.
Ca(+2a)
7 2 2.0 0.0 0.0 0.0 1.0 0.0 0.0 0.0 0.0 0.0 0.0 -2.0
-543083.20 -56.484000
333.15000 12429.700 -51.306780 0.59345610E-01 -.21681000E+09
0.00000000
473.15000 -1831.3110 7.7653710 -.95517030E-02 30467900.
CaCl(+a)
7 2 1.0 0.0 0.0 0.0 1.0 1.0 0.0 0.0 0.0 0.0 0.0 -1.0
-705451.70 18.8280000
333.15000 -284.96450 1.5453000 -.20419000E-02 7010438.0
0.00000000
473.15000 -796.32030 3.4969650 -.41311030E-02 17349180.
CaHCO3(+a)
7 1 1.0 1.0 3.0 1.0 1.0 0.0 0.0 0.0 0.0 0.0 0.0 -1.0
-1216000.0 119.39880
398.00000 0.00000000 0.38211930 0.00000000 0.00000000
Cd(+2a)
7 2 2.0 0.0 0.0 0.0 0.0 0.0 1.0 0.0 0.0 0.0 0.0 -2.0
-75897.760 -72.802000
333.15000 16746.400 -69.066780 0.80088500E-01 -.29223730E+09
0.00000000
473.15000 -1710.8100 7.5179000 -.93812970E-02 26641890.
CdCl(+a)
7 2 1.0 0.0 0.0 0.0 0.0 1.0 1.0 0.0 0.0 0.0 0.0 -1.0
-248496.10 3.138000
333.15000 -6446.0520 27.158630 -.31994360E-01 0.11586150E+09
0.00000000
473.15000 -1043.3070 4.3995720 -.50231900E-02 25538880.
CdCl3(-a)
7 2 -1.0 0.0 0.0 0.0 0.0 3.0 1.0 0.0 0.0 0.0 0.0 1.0
-606328.50 45.438000

333.15000 -29140.640 121.65980 -.14286000 0.51814120E+09
0.00000000
473.15000 -3230.7340 12.936520 -.14481410E-01 81248160.
CdCl4(-2a)
7 2 -2.0 0.0 0.0 0.0 0.0 4.0 1.0 0.0 0.0 0.0 0.0 2.0
-798277.90 0.9620000
333.15000 -28414.070 119.00600 -.14060520 0.50846500E+09
0.00000000
473.15000 -6254.0720 25.282690 -.29122460E-01 0.14130640E+09
Cl(-a)
7 2 -1.0 0.0 0.0 0.0 0.0 1.0 0.0 0.0 0.0 0.0 0.0 1.0
-167079.70 56.735000
333.15000 24068.930 -99.735470 0.11582300 -.42232760E+09
0.00000000
473.15000 -1949.4080 8.3394730 -.10566240E-01 26149870.
H(+a)
7 2 1.0 0.0 0.0 1.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 -1.0
0.00000000 0.00000000
333.15000 0.00000000 0.39120400 0.00000000 0.00000000
0.00000000
473.15000 0.00000000 0.39120400 0.00000000 0.00000000
HCO3(-a)
7 2 -1.0 1.0 3.0 1.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1.0
-689933.20 98.450000
333.15000 20291.630 -83.794550 0.97286460E-01 -.35478020E+09
0.00000000
473.15000 -1658.0410 7.3630430 -.92996350E-02 23715680.
Mg(+2a)
7 2 2.0 0.0 0.0 0.0 0.0 0.0 0.0 1.0 0.0 0.0 0.0 -2.0
-465959.50 -138.07200
333.15000 25030.970 -103.28210 0.11992740 -.43731870E+09
0.00000000
473.15000 -1965.4780 8.8457480 -.11190370E-01 28106590.
MgCl(+a)
7 2 1.0 0.0 0.0 0.0 0.0 1.0 0.0 1.0 0.0 0.0 0.0 -1.0
-631503.70 -79.49600
333.15000 -4497.0520 19.123810 -.22755010E-01 82010960.
0.00000000
473.15000 -1528.6680 6.4128230 -.74631790E-02 34213330.
Na(+a)
7 2 1.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1.0 0.0 0.0 -1.0
-240299.70 58.409000
333.15000 11370.860 -46.769460 0.54484670E-01 -.19836740E+09
0.00000000
473.15000 -197.03050 1.4005870 -.19819560E-02 -27187.630
O2(a)

7 1 0.0 0.0 2.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0
-11715.200 110.91780
398.00000 0.00000000 1.1598160 0.00000000 0.00000000
OH(-a)
7 2 -1.0 0.0 1.0 1.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1.0
-230023.80 -10.7110
333.15000 40928.520 -169.40110 0.19708960 -.71801180E+09
0.00000000
473.15000 -1918.4480 8.8302590 -.11628820E-01 18297730.
Pb(+2a)
7 2 2.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1.0 0.0 -2.0
920.48000 17.57300
333.15000 22685.800 -93.784260 0.10905300 -.39739380E+09
0.00000000
473.15000 -1258.1820 5.7726000 -.74849420E-02 14458090.
PbCl(+a)
7 1 1.0 0.0 0.0 0.0 0.0 1.0 0.0 0.0 0.0 1.0 0.0 -1.0
-161627.90 117.15200
298.20000 0.00000000 0.38581080 0.00000000 0.00000000
PbCl3(-a)
7 1 -1.0 0.0 0.0 0.0 0.0 3.0 0.0 0.0 0.0 1.0 0.0 1.0
-492456.80 246.85600
298.20000 0.00000000 -.77311950 0.00000000 0.00000000
PbCl4(-a)
7 2 -1.0 0.0 0.0 0.0 0.0 4.0 0.0 0.0 0.0 1.0 0.0 1.0
-666130.50 276.14400
333.15000 41879.690 -173.30550 0.20141440 -.73414980E+09
0.00000000
473.15000 -2760.5600 12.228680 -.15680860E-01 34362200.
Zn(+2a)
7 2 2.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1.0 -2.0
-153385.40 -109.62100
333.15000 19327.230 -79.748340 0.92469360E-01 -.33742350E+09
0.00000000
473.15000 -2003.9880 8.7579010 -.10923740E-01 31140750.
ZnCl(+a)
7 2 1.0 0.0 0.0 0.0 0.0 1.0 0.0 0.0 0.0 0.0 1.0 -1.0
-277148.20 96.232000
333.15000 -2843.6580 12.118250 -.14257400E-01 51662660.
0.00000000
473.15000 -364.30820 1.6909610 -.19190400E-02 10063080.
ZnCl3(-a)
7 2 -1.0 0.0 0.0 0.0 0.0 3.0 0.0 0.0 0.0 0.0 1.0 1.0
-632035.00 104.6000
333.15000 -15196.040 63.668410 -.74998460E-01 0.27160380E+09
0.00000000

```
 473.15000    -2506.5310     10.219730    -.11664310E-01  59409740.
2
4       11      0       2.6263926
2
4       11      1       13.418796
2
4       11      3       -0.00282676
2
4       18      0       -1.4524558
2
4       18      1       -1.9147142
2
4       18      2       -47.55608
2
4       13      0       3.3256
2
4       13      1       24.750778
2
4       21      0       0.133024
2
4       21      1       10.47564
2
4       22      0       -2.12007
2
4       22      3       0.2735306
2
19      11      0       2.16164
2
19      11      1       13.63496
2
19      11      3       0.731632
2
23      11      0       1.8974627
2
23      11      1       14.391534
2
23      11      3       -1.026779
2
7       11      0       0.13501936
2
7       11      1       3.6535873
2
7       11      2       0.0090622
2
14      11      0       2.9294379
2
```

14	11	1	13.979991
2			
14	11	3	0.04314966
2			
14	13	0	2.735306
2			
14	13	1	5.0482608
2			
14	21	0	1.74594
2			
14	21	1	8.97912
2			
14	22	0	-3.57502
2			
14	22	3	0.428171
2			
16	11	0	0.636021
2			
16	11	1	2.1982216
2			
16	11	3	0.01055878
2			
16	18	0	0.7183296
2			
16	18	1	2.103442
2			
16	18	3	0.0365816
2			
16	3	0	0.3317286
2			
16	3	1	11.548146
2			
16	3	3	0.0365816
2			
16	13	0	0.2302978
2			
16	13	1	0.3417054
2			
16	21	0	0.764888
2			
16	21	1	-5.4041
2			
16	22	3	-3.525136
2			
20	11	0	1.2471
2			

12	11	0	1.475735
2			
12	11	1	2.448473
2			
12	11	3	0.0066512
2			
12	21	0	2.24478
2			
12	21	1	-5.23782
2			
12	22	0	5.8198
2			
4	14	0	0.058198
3			
4	14	11	-0.099768
2			
4	16	0	0.58198
3			
4	16	11	-0.058198
2			
4	20	0	-0.99768
2			
4	12	0	0.764888
3			
4	12	11	-0.12471
2			
19	16	0	0.8314
2			
14	16	0	0.58198
3			
14	16	11	-0.099768
2			
14	20	0	-1.08082
2			
14	12	0	0.8314
3			
14	12	11	-0.091454
2			
16	20	0	-0.806458
2			
16	12	0	0.299304
3			
16	12	11	-0.033256
2			
11	18	0	-0.4157
3			

```
11      18      16      -0.049884
3
11      18      4       -0.20785
2
11      3       0       -0.16628
3
11      3       16      0.070669
2
11      13      0       0.24942
3
11      13      16      -0.12471
2
18      3       0       0.8314
3
18      3       16      -0.141338
2
3       13      0       -0.33256
3
3       13      16      0.016628
3
11      13      14      -0.798144
2
16      2       0       0.8314
2
4       2       0       1.521462
2
14      2       0       1.521462
2
11      2       0       -0.04157
0
CaCl2
 7 2  0.0  0.0  0.0  1.0  2.0  0.0  0.0  0.0  0.0  0.0  0.0
-795796.80      104.60000
 1045.0000      89.638020     -.33789980E-01 0.30790060E-04 -841820.80
 28543.250
 2273.0000      103.34480     0.00000000     0.00000000     0.00000000
 CaCl2*4H2O
 7 1  0.0  4.0  8.0  1.0  2.0  0.0  0.0  0.0  0.0  0.0  0.0
-2009136.0      272.19850
 398.00000      0.00000000     0.00000000     0.00000000     0.00000000
CaCl2*6H2O
 7 1  0.0  6.0 12.0  1.0  2.0  0.0  0.0  0.0  0.0  0.0  0.0
-2606101.0      354.43080
 398.00000      0.00000000     0.00000000     0.00000000     0.00000000
CdCl2
 7 2  0.0  0.0  0.0  0.0  2.0  1.0  0.0  0.0  0.0  0.0  0.0
```

-391496.90 115.26920
841.00000 70.073630 0.21966000E-01 -.12552000E-07 -182840.80
31798.400
1234.0000 111.29440 0.00000000 0.00000000 0.00000000
CdCl2*H2O
7 1 0.0 1.0 2.0 0.0 2.0 1.0 0.0 0.0 0.0 0.0 0.0
-686719.90 170.70720
398.00000 0.00000000 0.00000000 0.00000000 0.00000000
CdCl2*2.5H2O
7 1 0.0 2.500 5.0 0.0 2.0 1.0 0.0 0.0 0.0 0.0 0.0
-1129554.0 232.63040
398.00000 0.00000000 0.00000000 0.00000000 0.00000000
MgCl2
7 2 0.0 0.0 0.0 0.0 2.0 0.0 1.0 0.0 0.0 0.0 0.0
-641616.40 89.629650
987.00000 79.077600 0.59412800E-02 0.00000000 -861904.00
43095.200
1708.0000 92.048000 0.00000000 0.00000000 0.00000000
MgCl2*H2O
7 1 0.0 1.0 2.0 0.0 2.0 0.0 1.0 0.0 0.0 0.0 0.0
-966629.50 137.23520
650.00000 91.002000 0.81378800E-01 0.00000000 0.00000000
MgCl2*2H2O
7 1 0.0 2.0 4.0 0.0 2.0 0.0 1.0 0.0 0.0 0.0 0.0
-1279718.0 179.91200
500.00000 125.14340 0.11426500 0.00000000 0.00000000
MgCl2*4H2O
7 1 0.0 4.0 8.0 0.0 2.0 0.0 1.0 0.0 0.0 0.0 0.0
-1899034.0 264.01040
450.00000 187.56870 0.18003750 0.00000000 0.00000000
MgCl2*6H2O
7 1 0.0 6.0 12.0 0.0 2.0 0.0 1.0 0.0 0.0 0.0 0.0
-2499061.0 366.10000
385.00000 241.75150 0.24576820 0.00000000 0.00000000
NaCl
7 3 0.0 0.0 0.0 0.0 1.0 0.0 0.0 1.0 0.0 0.0 0.0
-411119.80 72.132160
1073.9500 57.262220 -.15484980E-01 0.23526630E-04 -378233.60
28158.320
1500.0000 77.763830 -.75312000E-02 0.00000000 0.00000000
0.00000000
2000.0000 66.944000 0.00000000 0.00000000 0.00000000
PbCl2
7 3 0.0 0.0 0.0 0.0 2.0 0.0 0.0 0.0 1.0 0.0 0.0
-359405.60 135.98000
774.00000 69.077840 0.27576740E-01 0.90374400E-06 -25522.400

21878.140
1225.0000 111.50360 0.00000000 0.00000000 0.00000000
0.00000000
2300.0000 111.00150 0.00000000 0.00000000 0.00000000
ZnCl2
7 2 0.0 0.0 0.0 0.0 2.0 0.0 0.0 0.0 0.0 1.0 0.0
-415052.80 111.46180
590.00000 62.939910 0.28664580E-01 0.00000000 0.00000000
10250.800
999.50000 68.412580 0.18639720E-01 0.21798640E-05 -243927.20
CaCO3
7 1 1.0 3.0 0.0 1.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0
-1206921.0 92.901540
1200.0000 99.667060 0.26965880E-01 0.00000000 -2154342.0
CdCO3
7 1 1.0 3.0 0.0 0.0 0.0 1.0 0.0 0.0 0.0 0.0 0.0
-751864.80 92.466400
600.00000 43.095200 0.13179600 0.00000000 0.00000000
MgCO3
7 1 1.0 3.0 0.0 0.0 0.0 0.0 1.0 0.0 0.0 0.0 0.0
-1095798.0 65.701350
700.00000 77.906080 0.57739200E-01 0.00000000 -1740544.0
Mg(OH)2
7 1 0.0 2.0 2.0 0.0 0.0 0.0 1.0 0.0 0.0 0.0 0.0
-924664.00 63.136560
900.00000 114.52030 -.17853130E-01 0.22426240E-04 -3022940.0
Na2CO3
7 3 1.0 3.0 0.0 0.0 0.0 0.0 0.0 2.0 0.0 0.0 0.0
-1130768.0 138.78330
723.00000 90.278170 0.16401280E-01 0.17505020E-03 26359.200
690.36000
1123.0000 50.082480 0.12907640 0.00000000 0.00000000
29664.560
2000.0000 142.21420 0.44768800E-01 0.00000000 0.00000000
NaHCO3
7 1 1.0 3.0 1.0 0.0 0.0 0.0 0.0 1.0 0.0 0.0 0.0
-950809.80 101.70050
500.00000 44.710220 0.14388780 0.00000000 0.00000000
NaOH
7 3 0.0 1.0 1.0 0.0 0.0 0.0 0.0 1.0 0.0 0.0 0.0
-425931.20 64.433600
572.00000 118.63730 -.25097310 0.35194550E-03 -1520047.0
7196.4800
596.00000 87.566940 0.00000000 0.00000000 0.00000000
6359.6800
1800.0000 90.453890 -.70500400E-02 0.43095200E-06 -112131.20

PbCO3
7 1 1.0 3.0 0.0 0.0 0.0 0.0 0.0 0.0 1.0 0.0 0.0
-699100.40 131.00100
800.00000 51.722610 0.11966240 0.00000000 0.00000000
ZnCO3
7 1 1.0 3.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1.0 0.0
-812779.70 82.399700
500.00000 38.911200 0.13807200 0.00000000 0.00000000
0


TEKNILLINEN KORKEAKOULU
LABOR SCIENTIA
KEMIAN TEKNIIKAN OSASTO